**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**THERMODYNAMIC STUDY OF ISOSTERIC HEAT AT
ZERO COVERAGE: APPLICATIONS TO ADSORPTION
COOLING AND DESALINATION**

**FAN WU
SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING
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ZERO COVERAGE: APPLICATIONS TO ADSORPTION
COOLING AND DESALINATION**

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Abstract

The production of cooling and drinkable water represents major and essential needs for the mankind. Vapor compression cooling and desalination systems are mainly driven by electricity, produced by burning fossil fuels, which contributes to the global warming (GW) because of the encountered direct CO₂-emissions. The refrigerants used in vapor compression systems possess high global warming potential (GWP), resulting in an indirect contribution to the GW and, consequently, to the severe consequences on the worldwide climate. Recovering the waste heat generated upon burning fossil fuels to provide both cooling and fresh water demands through the application of adsorption assisted cooling and desalination cycle may remarkably contribute in mitigating the bad consequences of the GW.

At present, the bulky size of adsorption chiller and desalination systems obstructs its practical application. The size of an adsorption bed depends on the quality of the porous adsorbents. Therefore, the present thesis aims to develop a thermodynamic framework for calculating the interaction potentials between the adsorbate and the adsorbent pore structures, from which the isosteric heat at zero coverage is formulated as a function of pore width and volume. The proposed modelling provides necessary information for the design of adsorbent materials.

The proposed interaction potential model includes the Lennard Jones (LJ) Potential with the inclusion of electrostatic and induction potential. The model is first applied to the graphite surface, in which the electrostatic and induction potentials are obtained to be very small compared to the LJ potential. The maximum isosteric heat is found in the super micro-pore regions. On the other hand, the Reverse Monte Carlo (RMC) and molecular dynamics methods are applied to understand the silica structure for water adsorption. For water interaction with silica gel, the electrostatic interaction is found to be high. For water adsorption on CHA and AFI

types zeolites, the most favourable adsorptive sites are identified at the positions of channels inside the zeolite frameworks.

A detailed experimental investigation is conducted for measuring (i) the amount of CO₂ uptakes on various activated carbons, and (ii) water uptakes on various types of silica gels and zeolites under static conditions. These isotherms data are fitted with isotherm models for their use in adsorption cooling and desalination modelling.

Employing the knowledge of isosteric heats, pore structures and isotherm data, a thermodynamic model is developed for calculating the energetic performances of adsorption cooling and desalination systems. From the present analysis, it is noticed that both graphite structure or activated carbon and silica gels are optimised with respect to pore sizes and volumes for given evaporating and heat source temperatures. The best performances of adsorption cooling and desalination cycles are obtained from a compromise between the greatest pore volume and the optimal pore size. From the present analysis, it is observed that there is no cooling and water production performance for pore widths varying from 0 to 0.3 nm. For better efficiency, the silica gel should be designed with a pore size from 1 nm to 2 nm for cooling application due to its higher coefficient of performance (COP). The average pore size of silica gel should be designed with 1 nm for the production of more water. On the other hand, for refrigeration purposes, the activated carbon should be designed with the average pore size ranging from 7 to 15 Å and higher micro-pore volumes.

This thesis thus provides some important information regarding the knowledge of isosteric heat at zero coverage for various adsorbent – adsorbate pairs, which can help in the design of new carbonaceous materials or carbon–silica or zeolites composites for adsorption assisted cooling and desalination purposes.

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3. Sun, B., **Fan, W.**, Chakraborty, A. Adsorption Kinetics Emulation with Lattice Gas Cellular. *Heat Transfer Engineering*. 2017, 38(4): 409-416.
4. Teo, H.W., Chakraborty, A., **Fan, W.** Improved adsorption characteristics data for AQSOA types zeolites and water systems under static and dynamic conditions. *Microporous and Mesoporous Materials*. 2017, 242: 109–117.

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1. Chakraborty, A., Sun, B., Ali, S.M., **Fan, W.** Design and Development Of Cryo-Adsorption Chamber for the Measurement of Methane Uptakes on Activated Carbons and MOFs. *Proceedings of the 7th Asian Conference on Refrigeration and Air Conditioning*, Jeju, Korea, 2014.
2. Sun, B., **Fan, W.**, Chakraborty, A., Adsorption Characteristics of Various MOFs for Gas Storage Applications. *The 6th International Meeting on Advanced Thermofluids*, Singapore, 2013.

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Nomenclature

Abbreviations

ads	adsorption
char	charging
cond	condenser
des	desorption
eff	effective value
evap	evaporator
rec	adsorption chamber
red	residual gas
sf	solid-fluid interface
sg	silica gel
wv	water vapor
ACAD	Adsorption Cooling and Desalination
AD	Adsorption Desalination
BET	Brunauer-Emmett-Teller Theory
BPE	Boiling-Point Elevation
COP	Coefficient of Performance
CVVP	Control Volume Variable Pressure
GCMC	Grand Canonical Monte Carlo
GW	Global Warming
GWP	Global Warming Potential
HDH	Humidification-dehumidification

HVAC		Heating Ventilation and Air Conditioning
IUPAC		International Union of Pure and Applied Chemistry
MOF	-	Metal Organic Framework
NIST	-	National Institute of Standards and Technology, USA
PID	-	proportional–integral–derivative
PR	-	Performance Ratio
REFPROP	-	Reference Fluid Thermodynamic and Transport Properties
RMC	-	Reverse Monte Carlo
SDWP	-	Specific Daily Water Production
XRD	-	X-ray Diffraction

Symbols

b	affinity constant	-
c	constant in adsorption isotherms	-
$c_{p,s}$	specific heat of sea water	J/(kg·K)
E_0	characteristic energy	kJ/mol
E_a	activation energy of adsorption	kJ/mol
h	heat transfer coefficient	W/(m ² ·K)
h_f	enthalpy of sea water	kJ/mol
k	thermal conductivity	W/(m·K)
k_a	adsorption rate constant	-
k_B	Boltzmann constant	J/K
K_F	constant for Freundlich adsorption isotherm	-
K_{LF}	constant for Sips adsorption isotherm	-

K_o	pre-exponential coefficient	-
K_T	constant for Toth adsorption isotherm	-
$\dot{m}$	mass flow rate	kg/s
m_{char}	mass of residue gas in charging chamber	kg
m_{eq}	equilibrium mass	kg
m_{init}	initial mass	kg
m_{LF}	heterogeneity parameter	-
m_{rec}	mass of initial residue gas in adsorption chamber	kg
m_{red}	mass of final residue gas in adsorption chamber	kg
M_s	mass of adsorbent	kg
m_{SG}	mass of silica gel	kg
M_t	total mass	kg
$1/n$	heterogeneity parameter	-
n_I	adsorbate-adsorbent interaction factor	-
P	pressure	Pa
P_{ads}	adsorption pressure	Pa
P_{dos}	dosing pressure	Pa
P_s	saturation pressure	Pa
q_{ads}	uptake during adsorption	kg/kg
q_{des}	uptake during desorption	kg/kg
q^o	the limiting uptake	kg/kg
q_{st}^o	Isosteric heat of adsorption at zero coverage	eV, kJ/mol, kJ/kg
q_t	uptake at time t	kg/kg

w	interaction energy between adsorbed molecules	kJ/mol
R	ideal gas constant	J/(mol·K)
t	constant for Toth adsorption isotherm	-
t_I	surface heterogeneity	-
T	temperature	K
U	potential	J
U_{LJ}	Lenard-Jones potential	J
U_E	electrostatic potential	J
U_I	induction potential	J
U_{mM}	total interaction potential	J
v_{ext}	total external potential	meV
v_{LJ}	Lennard –Jones potential	meV
v_E	Electrostatic potential	meV
v_I	Induction potential	meV
V_{char}	volume of charging chamber	m ³
V_{rec}	volume of adsorption chamber	m ³
V_{rec}	volume of adsorption chamber	m ³
z	the distance between adsorbent – adsorbate	Å
z_o	the distance for maximum q_{st}^o	Å
β	loading factor	-
ϵ_0	vacuum permittivity	C/(V·m)
ϵ	potential	J
ϵ_{ij}	pair well depth potential	J

θ	surface adsorbate coverage	-
μ	chemical potential	J/mol
ρ_{char}	density of gas during charging	kg/m ³
ρ_{rec}	density of residue gas	kg/m ³
σ	collision diameter	m
σ_{ij}	pair collision diameter	m
γ_A	coefficient of Lenard-Jones potential	-
γ_R	coefficient of LJ potential	-
ϕ_{dipole}	electrical potential of a dipole	V
ϕ_m	the minimum potential energy	J
$\phi_{quadrupole}$	electrical potential of a quadrupole	V
E	electric field vector	V/m
E _{dipole}	electric field vector of a dipole	V/m
E _{quadrupole}	electric field vector of a quadrupole	V/m
F	electric field vector	V/m
I	3×3 unit diagonal matrix	-
r	position vector between two multipoles	m
r ^T	transposed position vector	m
r _i	position vector of the <i>i</i> th atom of the adsorbate molecule	m
r _j	position vector of the <i>j</i> th carbon atom	m
r _{ij}	position vector from the <i>i</i> th carbon to the <i>j</i> th atom of the adsorbate molecule	m
α	polarisability matrix	Å ³

Θ	quadrupole moment matrix	DÅ
μ	dipole moment vector	D
μ^I	induced dipole moment vector	D
$\mu_{\text{H}_2\text{O}}^I$	induced dipole moment vector of water molecule	D
μ_{C}^I	induced dipole moment vector of carbon atom	D

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Chapter 1 Introduction

1.1 Background

Adsorption is the adhesion of particles (atoms, ions, molecules as adsorbate) to a porous surface of adsorbent while desorption is correspondingly a the reversible process [1]. The adsorption-desorption phenomena are generally employed for thermal compression processes for low temperature heat transmission applications such as adsorption cooling, desalination and dehumidification [2-4].

In an adsorption process as shown schematically in Figure 1.1, the motions of adsorbate molecules are restrained by binding forces between them in the pore surfaces, and the energy is

Figure 1.1 The schematic adsorption process

released to the environment due to the exothermic process [5]. On the other hand, due to the addition of heat or pressure swing, the trapped molecules in the pores escape in an endothermic process.

When the molecular motion of the adsorbate balances in the pores and surfaces of an adsorbent with respect to all directions of the adsorption pressure, adsorption equilibrium is achieved. Therefore, the lower temperature shifts the balance towards the adsorption process while the higher temperature accelerates the desorption process. Thus, the reversible adsorption-desorption process advocates a cyclic adhesion and release of the adsorbate from the porous solid adsorbent, and can be applied for the generation of low temperature heat transformation processes, i.e., cooling cycle. The low temperature occurs in the evaporator by amalgamation of adsorption-triggered-evaporation and desorption-activated-condensation [6].

The amount of adsorbate on a porous adsorbent under equilibrium conditions can be represented in a pressure-uptake (P - q) coordinate system at a constant temperature (T), which is known as an adsorption isotherm. The isotherm curves are essential for understanding the Henry and saturated regions of an adsorbent-adsorbate system. Practically, isotherms are presented through a collected set of experimentally measured data. The adsorption isotherm data are used to calculate the differential amount of refrigerant exchanged in each adsorption/desorption cycle for the design of adsorption assisted cooling, desalination, purification and gas storage systems. The isotherm classifications are based on the shape of adsorption isotherm curves ranging from Henry's region to the saturated pressure. At first, adsorption isotherms are classified into five BET types according to IUPAC classification as shown in Figure 1.2 [5, 7], where the x axis is the relative pressure (P/P_s , P and P_s are adsorption and saturation pressure in unit Pa) and the y axis is uptake (in unit g/g).

Figure 1.2 IUPAC Classifications of Adsorption Isotherms

Type I describes an adsorption process that mainly occurs in the microporous adsorbent with maximum loading under equilibrium conditions. Type II characterises the nature of adsorption uptake on a macroporous adsorbent with strong adsorbate-adsorbent interactions at relatively higher pressure. On the other hand, type III provides weaker interactions at the beginning of adsorption. For type IV isotherm, monolayer adsorption with capillary condensation is observed, and type V shows multilayer adsorption [8].

It should be noted that the adsorption kinetics quantitatively describes the dynamic behaviours of adsorbate uptakes on porous adsorbent for various temperatures and pressures. Generally, the porous solid with large surface area and micro-pore volume yields high uptakes while those with large pore networks are responsible for faster kinetics [5].

During an adsorption process, the adsorbate molecules are held near to the pores of the adsorbent surface and pores by van der Waals force fields, and the amount of adsorbed heat, mass of adsorbate and gaseous molecules and chemical potentials of adsorbed (μ_a) and the gaseous phases (μ_g) are necessary for fully describing the thermodynamic state of adsorbent - adsorbate systems. Adsorption isosteric heat (q_{st}) is defined as the difference between the energies

processed by the adsorbate molecules in both gaseous and adsorbed phases, as illustrated schematically in Figure 1.3 [9].

Figure 1.3 The schematic formalism of adsorption isosteric heat

The knowledge of isosteric heat at zero coverage (q_{st}^0) is necessary for calculating the energetic performances of adsorption assisted cooling, desalination and gas storage [10-12]. At zero surface coverage, the density of adsorbate molecules in the adsorbent pores and surface is relatively very low and the pressure is considered close to zero (not zero numerically, $P \rightarrow 0$), which allows the adsorbate–adsorbate interactions to be negligible. It should also be noted here that the modelling of (q_{st}^0). at higher pressure is complicated due to the presence of intermolecular interactions along the adsorbates. The modelling of q_{st}^0 has been studied by molecular simulations for many commonly applied adsorbent and adsorbate pairs [13, 14].

A good number of adsorption isotherm models are proposed on the basis of either the mechanism of adsorption processes or the curve-fitting results that are best matched with experimental data [5, 15]. Both first and second order adsorption kinetics are also used for the analysis of adsorption experimental data, modelling and simulation [11, 16, 17]. These adsorption isotherm and kinetics results are made to be conveniently ready-to-use by the simulation of the isosteric heat of adsorption. However, there has been a lack of theoretical explanation for the formalism of the isosteric heat of adsorption. Therefore, a thermodynamic study of isosteric heat at zero coverage would be essential from a theoretical point of view.

In the arena of adsorption cooling and desalination systems, the basic characteristics such as adsorption isotherms, kinetics and isosteric heats are commonly used to quantitatively describe their thermodynamic performances employing the mass and energy balances [10, 11, 18].

The adsorption assisted cooling and desalination systems are scalable, nearly free of moving parts, environmentally friendly and driven by the low grade waste heat (temperatures are ranged from 55 °C to 90 °C). The conventional vapour compression cooling system utilises non-natural refrigerants (such as R132a, R507a, R410, R1234yf etc.) [19]. On the other hand, the thermally-driven adsorption cooling employs natural refrigerants (e.g., water, ammonia), and can be conveniently integrated with the currently used cooling cum desalination systems where the waste heat source from a co-generation system (such as power plant [20], internal combustion engines [21, 22], solar systems [23, 24], etc) are used without extra energy consumption. Secondly, the adsorption device employs solid adsorbents for the design of thermal compressor or sorption bed where the refrigerant (water vapour) is adsorbed and desorbed to transfer water vapour from evaporator to bed and from bed to the compressor per adsorption-desorption cycle. The other heat driven cooling system such as absorption chiller utilises liquid desiccant-solution

for producing cooling by absorption-triggered-evaporation and solution regeneration-activated-condensation [25]. The conventional absorption chiller requires very high regeneration temperature ($> 100\text{ }^{\circ}\text{C}$) and LiBr or LiCl solutions are toxic. It should be noted here that the adsorption desalination systems as an emerging thermally-driven method are proved to be energy efficient and environmentally friendly due to its ability to produce high-grade potable water and cooling effects with only a single heat source input of $80\text{ }^{\circ}\text{C}$ or lower [26].

1.2 Motivation

In this thesis, the theoretical insight of isosteric heat of adsorption at zero coverage will be focused.

Since a good number of experimentally measured isosteric heat of adsorption data for adsorption of graphite and polar molecules, activated carbon and carbon dioxide, silica gel and water, zeolites (AQSOA-Z01, Z02 and Z05) and water systems are available in literature, a theoretical analysis for predicting the isosteric heat of adsorption at zero coverage (q_{st}^0) has to be developed. The isosteric heat of adsorption at zero coverage is closely related to the structure of adsorbent materials. The adsorbent structure analysis is also simulated theoretically to understand its pore size and volume. The combination of adsorbent structure and the interaction potential between adsorbent and adsorbate are necessary to calculate the isosteric heat of adsorption and also to predict the energetic performance of adsorption cooling and desalination systems.

The value of isosteric heat of adsorption at zero coverage can significantly influence the performances of adsorption assisted cooling and desalination cycle as a function of pore width of adsorbent materials. Therefore, the knowledge of isosteric heat of adsorption is needed to design the adsorption bed.

1.3 Research Objectives and Scope

This thesis aspires to develop a theoretical foundation to calculate the isosteric heat of adsorption at zero coverage for various adsorbent and adsorbate systems. Employing the theoretical formulation of isosteric heat, the energetic performances of adsorption cooling and desalination systems are predicted in terms of the pore width and volume of adsorbent materials. A connection has been established between adsorbent structures and the adsorption energy from a thermodynamic perspective.

These objectives are achieved by including the following research activities:

1. To construct structure models of adsorbents and adsorbates based on crystallography knowledge of various types of interfaces including lattice, amorphous surface and frameworks.
2. To investigate various interaction potentials such as Lennard-Jones, electrostatic and induction between adsorbate molecules with the constructed adsorbent structures.
3. To develop the thermodynamic formalism of isosteric heat as a function of pore width.
4. To investigate experimentally the amount of water vapour and CO₂ uptakes on silica gel, zeolites and activated carbons for the temperatures ranging from 25 to 65 °C and pressures up to 10 kPa under both static and dynamic conditions.
5. To conduct a numerical analysis for calculating the performances of adsorption cooling and desalination systems in terms of COP and specific daily water production employing the proposed formulations and experimentally measured isotherm data.

1.4 Outline of report

This thesis starts with a brief introduction about the background, motivations and objectives to be achieved from the proposed research. These are illustrated in Chapter 1.

Chapter 2 reviews the literature and introduces the state of the arts of research works related to the topics, including various types of cooling technologies, desalination technologies, the adsorption phenomenon, isotherms and kinetics, the principle of adsorption cooling-desalination cycles and the modelling and simulative researches of adsorption chiller and desalination. An integrated technical route is proposed to achieve all the research objectives based on the literature review.

Chapter 3 focuses on the modelling and simulation of isosteric heat of adsorption at zero coverage for various adsorbent + adsorbate systems. In this chapter, the molecular models of adsorbate materials and adsorbent are constructed, and the interactions between the adsorbent molecules with the constructed molecular models are studied. The values of isosteric heat for these pairs are then developed based on the calculation of interaction potential and pore model.

Chapter 4 presents the simulation results of the potential well and isosteric heats as a function of pore width for various orientations of adsorbate molecules, which is new.

Chapter 5 describes the detailed procedures of experimental study for the measurement of adsorption isotherm and kinetics for various adsorbent/adsorbate pairs.

Chapter 6 presents the performance evaluations of adsorption cooling and desalination systems in terms of COP and SWP as a function of pore width. These results are compared with experimentally measured data for verification purposes.

Chapter 7 concludes the findings of the current research and the directions of future work to improve the design, modelling and optimisation of adsorption beds for cooling and desalination purposes.

Chapter 2 Literature Review

2.1 Introduction

Firstly, the phenomenon of adsorption is described in detail from the viewpoints of adsorption isotherm and kinetic models. The explanation related to the theoretical development and understanding on adsorption isotherms and kinetics are provided here.

Secondly, the state of the art of simulation and theoretical formalisms of isosteric heat of adsorption will be given for various adsorbent + adsorbate pairs, which will provide some valuable insights on the constructions of connection between isosteric heat and the structure of porous adsorbents.

Thirdly, some novel cooling technologies being researched, such as CO₂ cooling are introduced and their advantages are discussed in order to elucidate the beneficial properties of these novel cooling technologies on concerns of environmental protection and economic efficiency.

Fourthly, a number of adsorption cooling and desalination systems are introduced. A brief description on these technologies is summarised.

2.2 Adsorption Isotherms and Kinetics

The adsorption isotherms and kinetics that characterise the equilibrium uptakes and adsorption rates are important properties of adsorption phenomenon in the modelling and simulation of adsorption cycles. During the history of more than a century, a good number of adsorption isotherms and kinetics models were derived and established.

The ideal isotherm models for monolayer adsorption are furnished in Table 2.1[5].

Table 2.1 Ideal isotherms for monolayer adsorption

Type	Isotherm	Remarks
Henry	$bP = \theta$	Applicable at Henry Region (low pressure range)
Langmuir	$bP = \frac{\theta}{1 - \theta}$	Localized and homogeneous adsorption is assumed.
Volmer	$bP = \frac{\theta}{1 - \theta} \exp\left(\frac{\theta}{1 - \theta}\right)$	The mobility of adsorbed molecules is allowed while the interaction is not.
Fowler-Guggenheim	$bP = \frac{\theta}{1 - \theta} \exp\left(\frac{-cw\theta}{RT}\right)$	The interaction is considered while mobility is not.
Hill-deBoer	$bP = \frac{\theta}{1 - \theta} \exp\left(\frac{\theta}{1 - \theta}\right) \exp(-c\theta)$	Both mobility and lateral interaction among adsorbed molecules are considered.

* b is affinity constant that measures how strong an adsorbate molecule is attracted onto a surface.

** $c = \frac{zw}{RT}$, where z is coordination number, w is interaction energy between adsorbed molecules, R is gas constant and T is the temperature.

The widely applied theoretical multilayer adsorption isotherms include the BET (Brunauer–Emmett–Teller) isotherm [27] and it is later extended to finite width, n -number of layers [7, 28].

The MacMillan–Teller (MET) isotherm [29] is an adsorption model similar to the BET isotherm that takes surface tension effects into consideration. Another well-known multilayer adsorption isotherm is the FHH (Frenkel-Halsey-Hill) isotherm [30-32]. The theoretical isotherm that fits multiple types of isotherm according to IUPAC is proposed to overcome limitations of existing isotherm model [33, 34], which also explains the surface energy and surface structural heterogeneity factors. Based on experimental data, empirical adsorption isotherms can be obtained through methods such as curve fitting. Some frequently applied empirical isotherms for monolayer adsorption are given as in Table 2.2 [15].

Table 2.2 Empirical isotherms for monolayer adsorption

Type	Isotherm	Remarks
Freundlich	$\theta = K_F P^{1/n}$	The earliest non-ideal and reversible adsorption isotherm not restricted to the formation of monolayer.
Dubinin–Radushkevich	$\theta = \exp \left[- \left(\frac{RT \ln(P_s/P)}{\beta E_0} \right)^2 \right]$	Successfully fits high solute and intermediate range of concentration but not applicable at Henry region.
Toth	$\theta = \frac{K_T P}{[1 + (K_T P)^t]^{1/t}}$	Useful in heterogeneous adsorption systems with satisfactory low and high-end boundary of concentrations.
Langmuir- Freundlich (Sips equation)	$\theta = \frac{(K_{LF} P)^{m_{LF}}}{1 + (K_{LF} P)^{m_{LF}}}$	It reduces to Freundlich isotherm at low pressure area and Langmuir isotherm at high pressure area.

*Exponential items such as $1/n$, m_{LF} are the heterogeneity parameter that characterises the width and asymmetry of the distribution $\chi(\varepsilon)$ [35, 36].

Although they provide no information about the chemical or physical mechanism of adsorption and the parameters used in the isotherms are only valid for particular experimental conditions, these empirical isotherms that are obtained through curve fitting have high precision in specific pressure range [37]. Therefore, these isotherms that are verified with experimental data have been widely applied in the modelling and simulation of adsorption processes.

The adsorption kinetics defines the variation of uptake of a specific adsorbent + adsorbate pair against time until the adsorption equilibrium is thermodynamically achieved [5]. It characterise the speed of a adsorption process, which can be measured by adsorption experiments. The adsorption kinetics are important as the diffusion of adsorbed particles on adsorbent is applied in catalysis, metallurgy, microelectronics, material science, etc[1].

The pseudo first-order kinetic model as proposed by Lagergren is derived based on the assumption that the adsorption rate is proportional to the number of unoccupied adsorptive sites [38], and the equation is given by

$$\frac{dq_t}{dt} = k_1(q^o - q_t) \quad (2.1)$$

, where q^o and q_t are the adsorption capacities at equilibrium and time t , $(q^o - q_t)$ represents to the number of unoccupied adsorptive sites and k_1 is the constant of pseudo first-order adsorption and it yields

$$\log(q^o - q_t) = \log(q^o) - \frac{k_1}{2.303} t \quad (2.2)$$

The second order adsorption is obtained by applying a second order adsorption rate as [39, 40].

$$\frac{dq_t}{dt} = k_1(q^o - q_t)^2 \quad (2.3)$$

which also shows

$$\frac{t}{q_t} = \frac{1}{k_2(q^o)^2} + \frac{1}{q^o} t \quad (2.4)$$

The relationship between adsorption rate constant k_a and temperature T is represented in an Arrhenius form

$$k_a = k_0 \exp\left(-\frac{E_a}{RT}\right) \quad (2.5)$$

where k_0 is the temperature independent factor, E_a is activation energy of adsorption, R is the ideal gas constant and T is absolute temperature [16, 41].

Both first and second order adsorption kinetics have been used in the analysis of adsorption experimental data, modelling and simulations [11, 16, 17].

2.3 Isostatic Heat of Adsorption

The isosteric heat of adsorption describes the energetic performances of an adsorption process in a pressure-temperature-uptake coordinate system employing the Clausius - Clapeyron equation. Up to now, a thermodynamic framework describing the isosteric heat of adsorption with respect to adsorbent structure and adsorbate orientation is not well established. It should be noted here that the basic concept of calculating the isosteric heats employing the Grand Canonical Monte Carlo simulation is well established. A summary of the simulation techniques for the isosteric heat of adsorption is furnished in Table 2.3

Table 2.3 Summary of isosteric heat of adsorption for various adsorbent – adsorbate pairs

Adsorbent+adsorbate pair	Adsorbent Structure	Interaction Potential	Remarks
Silica gel + water [6]	Layers of silicon and oxygen atoms + parallel slit-shaped pore model	Steele's 10-4-3 Lennard-Jones interaction potential	Clausius–Clapeyron equation is applied to Henry's region
Carbon + N ₂ , Ar, CO ₂ , CH ₄ , He, H ₂ [13]	Layers of graphite lattice + parallel slit-shaped pore model	Steele's 10-4-3 Lennard-Jones interaction potential	Clausius–Clapeyron equation is applied to Henry's region
Graphite + CO, HCN, H ₂ C O and H ₂ O [42]	Layers of graphite lattice	Energy expansion formulation	Approximate energy required to keep the molecule with thermal energy $\left(\frac{n}{2} + 1\right) kT$ at its equilibrium configuration on the surface of the substrate
Graphite + H ₂ O, CH ₃ CH ₂ OH [43]	Layers of graphite lattice	Steele's 10-4-3 Lennard-Jones + electrostatic interaction potential	Partial derivative of system energy on adsorbed particle number in Grand canonical Monte Carlo (GCMC) simulation plus kT
Graphitized carbon black + CH ₃ OH, CH ₃ CH ₂ OH [44]	Layers of graphite lattice + parallel slit-shaped pore model	Steele's 10-4-3 Lennard-Jones + electrostatic interaction potential	Partial derivative of system energy on adsorbed particle number in Grand canonical Monte Carlo (GCMC) simulation plus kT

In these simulations, simple parallel slit-shaped pore model and Steel's 10-4-3 interaction potential models are commonly used to calculate the adsorbate-adsorbent interaction potential and the external wall potential. The Clausius–Clapeyron equation is then applied to the Henry's region to develop a deterministic relationship between the isosteric heat and the pore width.

For calculating the isosteric heat of adsorption at higher pressures, where adsorbate-adsorbate interactions can no longer be ignored, a GCMC simulation based on probabilistic method is widely applied. Therefore, to construct a more structured model than the simple slit-shaped pore model is necessary.

2.4 Adsorption Assisted Cooling and Desalination

Generally, an adsorption assisted cooling and desalination system will consist of evaporators, adsorption and desorption beds, condenser and auxiliary subsystems as shown in Figure 2.1

Figure 2.1 Schematic of adsorption cooling and desalination system

Employing silica gel and water as the working pair, liquid water is firstly vaporised in the evaporation chamber with the heat from a heat exchanger inside it. The generated water vapour is then charged into the adsorption bed during the adsorption process. Water vapour is then adsorbed at the adsorption bed by adsorbent. The adsorption/desorption temperature is maintained by an internal heat exchange subsystem with cold/hot water supply. After a specified half-cycle, the adsorption process is switched off and then the desorption process starts. Similar to adsorption process, adsorbed water in the previous adsorption half-cycle is released from the adsorbent. After another half-cycle, the desorption process is switched off and then the adsorption process starts again. During the switching period, the system will reverse the cooling and hot water supply so as to preheat and precool the beds for the next half-cycle. On the other hand, the released water vapour at desorption process is charged into the condenser with an internal heat exchange subsystem. Water vapour is cooled, condensed to liquid water and finally collected in a water collection tank. These two adsorption and desorption half-cycles together with two switching periods become a whole working cycle for the adsorption assisted cooling and desalination cycle.

The performance parameter of adsorption cooling cycle is defined by the coefficient of performance (COP) i.e. (Q_{evap}/Q_{des}) [10], where Q_{evap} and Q_{des} are cooling capacity and the amount of heat added to the sorption bed during desorption stage. The overall performance ratio (OPR) is given by $(Q_{evap} + Q_{cond})/Q_{des}$ [45]. The specific cooling power (SCP) is the ratio of the cooling power to the total mass of adsorbent (i.e. Q_{evap}/M_s in unit: W/kg, M_s is the mass of adsorbent) [46]. The performance for adsorption desalination system is defined by specific water production (SWP) and Specific Daily Water Production (SDWP). SWP is calculated as $(q_{ads} -$

q_{des}) and $SDWP = \int_0^{t_{cycle}} \frac{Q_{cond}}{h_{fg}M_s} dt$, where t_{cycle} is the cycle time, Q_{cond} is condensation heat of the condenser and h_{fg} is the enthalpy of adsorbate[47].

The adsorption cycle has been investigated and applied in cooling systems by many researchers because it is environmentally friendly, free of moving parts, scalability etc. In a conventional adsorption chiller, both the macro and micro-porous silica gels are housed in the copper-fin-tube heat exchanger of adsorption bed to improve the heat and water vapour transfer [48]. Therefore the cooling capacity and COP are increased. The cascade cooling cycle can also be designed by combining two adsorption cooling cycles of zeolite and silica gel as adsorbents respectively [49]. By replacing water with saline in the evaporator, the adsorption cooling cycle can be integrated with desalination and thus creates the Adsorption Desalination (AD) cycle. The advanced AD cycle, an improved adsorption cycle where the heated water in internal heat exchanger of condenser is circulated to that of the evaporator to recover the condensation heat, has been proposed to increase the Specific Daily Water Production (SDWP) of an adsorption desalination system [3, 17, 47]. The mathematical models are proposed based on the isotherm and kinetics of the adsorbent/adsorbate pair to simulate the energy and mass balances for the each component of the cycle [4]. A numerical model on advanced adsorption desalination cycle has been developed by [50] to analyse the system performance.

Adsorption can also be combined with other cooling technologies such as CO₂ cooling as gas cooler to recover waste heat. The simulation and experiments of the combined cooling cycles are reported to have a higher COP than only a single cooling cycle [51, 52]. Adsorption is designed to combine with solar energy as a refrigeration cycle at tropical climate [53]. In one study by Habib et al. [54], the adsorption refrigeration comprises two cycles, where the bottoming cycle

of activated carbon (AC)-R507A is combined with the topping cycle of AC-R134a and the novel refrigeration cycle can provide $-10\text{ }^{\circ}\text{C}$ cooling temperature at the bottoming cycle.

2.4.1 Adsorption Cooling

A review of adsorption cooling systems utilising various adsorbent+ adsorbate pairs, system configuration, adsorption isotherm, adsorption kinetic together with system performances by simulation and experimental investigations are summarised in Table 2.4 The Cooling performances of these systems have been studied with various adsorbent+ adsorbate pairs such as silica gel + water, zeolite + water, zeolite + methanol, CaCl_2 /activated carbon + ammonia, activated carbon + CO_2 , silica gel/LiCl + methanol, and novel composite adsorbent + water.

The theoretical research on adsorption cooling devices currently focuses on mathematical modelling including lumped and distributed modelling that can accurately depict system status at given operational conditions. Optimal operation parameters can be discovered in the optimisation of the cooling performance based on the system modelling. Furthermore, the modelling research can be verified by experimental investigations and also guide the design of adsorption cooling systems [55].

Table 2.4 Summary of Adsorption Cooling Systems

Adsorbent+adsorbate pair	Description	Characteristics	Performance
Silica gel(RD type) +water[56]	Two bed adsorption chiller simulation with lumped modeling	Modified Henry's isotherm and LDF kinetic equations	Lumped modelling is less accurate than the distributed modelling and the difference is less than 10% in temperature profile
Silica gel (RD type and A type)+water[57]	Two bed adsorption chiller. Distributed modelling is applied	Tóth isotherm and near-exponential kinetics [58]	Smaller grain size and layer with higher COP
Silica gel(RD type and CaCl ₂ in silica gel) +water[59]	Two bed adsorption chiller with lumped + distributed modelling	Modified Freundlich isotherms for RD type silica gel plus water. Tóth isotherm for CaCl ₂ in silica gel LDF kinetics model	Temporal history of the AD chiller. Cooling capacity is increased by 6%
Zeolite +water[60, 61]	Two bed adsorption chiller Lumped modeling Experimental investigation	Equilibrium uptake LDF kinetics model	COP ranges from 0.1 to 0.6 Optimal operation temperature and cycle time are obtained for best COP
Zeolite+ methanol[62]	Adsorption chiller analysis with experimental investigation	Various operation conditions to test the potential application	Temperature profile and specific cooling power are obtained COP ranges from 0.1 to 0.12
LiCl in silica gel+methanol[63]	Two bed adsorption chiller is experimentally investigated	Employing both heat and mass recoveries	The SCP and the COP are improved by 16.3% and 24.2% as compared with silica gel+water assisted chiller
Activated carbon fiber+ethanol[64]	Two bed adsorption chiller Lumped modeling	Dubinin–Radushkevich (D–R) isotherm and LDF kinetics model	Temperature profile and Dühring diagram are depicted
Activated carbon+CO ₂ [65]	Four bed adsorption cooling Lumped modeling	Tóth isotherm and experimental data LDF kinetics models	Temperature profiles with P-T-X and P–h diagram COP against cycle time

CaCl ₂ /activated carbon + ammonia Silica gel/LiCl+methanol [55]	Two bed refrigerator Two bed adsorption chiller and experimental investigation	Constant evaporating temperature Both heat and mass recoveries methods	Clausius Clapeyron diagram of CaCl ₂ /activated-ammonia for adsorption refrigeration. P-T-X diagram of silica gel/LiCl-methanol adsorption chiller
Novel composite adsorbent (activated carbon soaking in Na ₂ (SiO ₂) _n O and CaCl ₂ solution) +water[66]	Descriptions of two bed adsorption chiller with experimental investigation	Isotherm from experimental result[67] LDF kinetics model is employed	Composite adsorbents are used for the average SCP of 378 W/kg and the COP of 0.7

2.4.2 Adsorption Desalination

Adsorption desalination results from the unique union of evaporation and condensation through adsorption and desorption. A review of adsorption desalination systems with various adsorbent + adsorbate pairs, system configurations, and dynamic performances is summarised in Table 2.5. The performances of various adsorption desalination systems are specified by the performance ratio (PR) and specific daily water production (SDWP).

Table 2.5 Summary of Adsorption Desalination Systems

Adsorbent +adsorbate pairs	Descriptions	Characteristics	Performances
Silica gel (RD type) +water [68]	Two bed adsorption chiller Desalination employing distributed modelling and experimental investigations	Linear adsorption isotherm[69] LDF kinetics	Modelling is validated with experimental data for errors less than 5% Optimal cycle time is identified for best specific water production
Silica gel (RD type) +water [70]	Four bed adsorption chiller Two stage Lumped modelling	Tóth isotherm LDF kinetics	Novelty of inter-stage pressure as optimisation parameter

Silica gel (A ⁺⁺ type) + water [4, 17, 71]	Four bed advanced AD cycle with heat recovery* Lumped modelling	Dubinin-Astakhov (D-A) adsorption isotherm modelling	SDWP to hot water/cooling water inlet temperature SDWP varies from 8.1 to 26 m ³ per tonne of silica gel per day
Silica gel + water [50]	Two bed AD cycle integrated with evaporator and condenser Lumped modeling	Dubinin–Astakhov (D-A) LDF kinetics equation	Temperature, pressure profile P–T–C diagram of AD cycle The SDWP against cycle time, varies from 8.1 m ³ to 26 m ³
Silica gel +water [72]	Two bed and four bed mode Experimental investigation	Tóth isotherm and LDF kinetics model	Optimal performance parameters such as SDWP and PR are simulated and compared with experimental data
Silica gel + water MED [73-75]	Two bed AD cycle hybrid with Multi Effect Distillation (MED) Lumped modelling	Tóth isotherms and LDF kinetics models for simplicity	MED + AD increases water production more than 3 folds as compared to traditional MED plants.

*In an advanced adsorption desorption (AD) desalination cycle, the internal latent heat between the evaporator and the condenser units is recovered and also is equivalent to that with a compressor to pressurise the adsorbent during adsorption, and thus making the adsorbent with a higher water vapour uptake [47].

It has been pointed out that the conventional desalination devices such as Multi-Stage Flash (MSF), Multi-Effect Desalination (MED), solar distillation, reverse osmosis (RO) and the electro-dialysis suffer from desalination shortcomings with the difficulties of maintenance, relatively high energy consumption and also high cost [26]. The water quality of adsorption desalination process is independent of high feed salinity in the evaporator and the chemical quality of desalinated water is comparable to deionized water quality [76]. Adsorption desalination can meet the need for desalination systems with low energy and running cost.

2.5 Summary

In this chapter, the literatures related to the proposed research objectives and scope are reviewed. The adsorption phenomena together with adsorption isotherms and kinetics models are introduced to offer a clear theoretical and empirical development for the quantitative prediction of adsorption isotherms and kinetics, which will later be applied in the modelling and simulation of isosteric heat as well as adsorption chiller. The widely applied pore models, interaction potentials models for various adsorbent-adsorbate pairs in the simulation of isosteric heat are listed. Several novel cooling and desalination technologies are introduced to highlight the advantages of adsorption process regarding the environmental and economic concerns about cooling and desalination systems. Finally, the descriptions and performances of some adsorption cooling and desalination systems are presented to prove the potential applications of adsorption. The next chapter begins with a theoretical insight of isosteric heat at zero coverage.

Chapter 3 Modelling and Simulation of Isosteric Heat of Adsorption at Zero Coverage

3.1 Introduction

Generally, the modelling of the adsorbate and adsorbent structures are needed in the first place in order to calculate the interaction potential and isosteric heat of adsorption at zero coverage (q_{st}^o). These parameters can also be expressed as a function of pore width. All these information are needed to design adsorption beds for adsorption cooling, desalination or gas storage [13, 77-82]. In this chapter, the adsorbents of lattice, amorphous and framework structures are described to understand the nature of adsorption interactions with various adsorbate molecules.

Graphitised carbon has a honeycomb lattice with a simple pore structure. It is well known that the potential energy and q_{st}^o provide important information about the adsorption mechanism ranging from Henry's region to the saturated pressure. Unlike covalent-network solids such as graphite, silica has an amorphous structure without a periodic, crystal-like surface such as silica gel. Silica gel is a form of highly porous amorphous silica (SiO_2) and is made from anhydride of silicic acid. Amorphous silica (a- SiO_2) is formed with $\text{Si}(\text{O}_{1/2})_4$ tetrahedrons which are connected by oxygen atoms [83]. Unlike the quartz crystal with a repeated unit cell in the molecular structure, the number of Si atoms in the ring of $\text{Si}(\text{O}_{1/2})_4$ tetrahedrons may differ from 2 to 8 due to the amorphicity of silica [84-86]. The length of the Si-O covalent bond is 1.61 Å [87] and its dipole moment is 3.098 D [88]. The difference between Si and O atoms is less than 1.7 in the Pauling electronegativity scale. The structure also possesses 50% of ionic character and 50% covalent character of Si-O bond. It should be noted here that framework structures such as zeolites [89, 90] are three-dimensional, highly porous, crystalline inorganic materials. The

structural instability of alumino-phosphate zeolite formed by TO_4 tetrahedral ($\text{T} = \text{Al}, \text{P}$ in an alternative manner) has limited its applications [91]. Therefore, other elements such as Si and Fe are incorporated into alumino-phosphate framework to generate more stable silico-alumino-phosphate, ferroaluminophosphate, etc. [92]

In this chapter, a thermodynamic framework is presented to calculate the binding energies of adsorbate molecules on various adsorbent structures such as graphite basal plane, amorphous silica gel and CHA and AFI type zeolite framework structures. The proposed modelling employs the static molecular model, where the Lennard-Jones (LJ), electrostatic and induction potentials are considered. The potential energy surfaces are presented with respect to various orientations of polar adsorbate molecules. Employing the derived potential model, the isosteric heat of adsorption is calculated as a function of pore width H .

3.2 Previous Studies on Adsorbent Structures and Modellings

Adsorption of gases and liquids on graphite surfaces was extensively studied [13, 80-82] as the system comprising graphite and polar or non-polar adsorbate provides a bench mark to evaluate molecular models such as Grand Canonical Monte Carlo (GCMC) and molecular dynamics (MD). However these methods are complex and require very high computational speed to calculate the amount of adsorbate uptake, kinetics and isosteric heat of adsorption. Therefore, for simplicity, a static molecular simulation technique will be applied to calculate the interaction potential and the isosteric heat of adsorption at zero coverage (q_{st}^0).

The interactions of adsorbate molecules on a graphite surface are analysed by intermolecular potential models to determine the binding energies [80]. Among the basic intermolecular potential models, the Lennard-Jones (LJ) potential model of molecules with weak long range attraction and strong short range repulsion [93] has been applied to predict the maximum binding

energies. The pair-wise additive L-J potential model between oxygen and carbon has been widely employed to the simulation of molecular dynamics of water and graphite systems [80]. Besides the interactive force between adsorbate and adsorbent molecules, the lateral attraction force between adsorbed molecules is reported to be positively strong on most homogenous, graphitised carbon surfaces whether the adsorbate molecule is polar or non-polar [94].

The Continuous Random Network (CRN) model was firstly proposed to describe the structure of amorphous semiconductors [95]. Based on the CRN model, the construction of amorphous silica structure was made from the diamond structure with periodic boundary conditions by Wooten, Winer and Weaire [83, 96, 97], which is known as WWW method. By randomly and repeatedly transposing the Si-Si bond in amorphous Si, a continuous random network can be generated while the tetrahedral coordination of each atom is preserved. The crystalline state is partially preserved after random operations due to the memory of initial configuration according to WWW model [98]. Therefore, a structural modelling technique namely Reverse Monte Carlo (RMC) method based on experimental data is developed to describe the structure of non-crystalline materials [99]. The RMC method is applied to the model of the molecular structures of amorphous silica [100] and silicon [101], which are consistent with available experimental data.

The adsorption of water onto silica gel ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) is considered as the interaction of H_2O molecule with the surface of amorphous silica structure for simplicity. For non-bonded interaction, the van der Waals and the electrostatic interactions are the main effects to determine the interaction potential. The interaction of $\text{H}_4\text{SiO}_4\text{-H}_2\text{O}$ pair is studied and applied to the molecular dynamics simulation to understand the adsorption of water on silica surface [82]. The residual hydroxyl group on the surface of silica is also considered in these simulation studies [96,

102]. The Born–Mayer–Huggins pair-wise potential model is applied in the simulation of adsorption of water on silica and silicate glass fracture surfaces [103]. It should be noted here that the calculation of q_{st}^0 for the adsorption of water on CHA and AFI type zeolites such as AQSOA-Z01, AQSOA-Z02 and AQSOA-Z05 are not available in the literature. In the next section, the modelling of q_{st}^0 based on molecular dynamics is presented in detail.

3.3 Molecular Models

The adsorption potential model integrates LJ, electrostatic and induction potentials, which takes into account dipole-dipole, dipole-quadrupole and dipole-induced dipole interactions. Therefore, the predicted interaction potential is more accurate than those that consider only LJ and charge-charge interactions according to the energy expansion equation. Previously, the multilayer LJ potential equation was applied as the interaction potential equation to predict the q_{st}^0 of adsorption for non-polar molecules in the parallel slit pore model [13, 104]. Instead of the widely adopted approximation of multilayer LJ potential [105], the present work applies the integrated and deterministic interaction potential. For simplicity, the parallel slit model is used for predicting q_{st}^0 as a function of pore width for some specific orientations. The interaction between adsorbate molecules is as important as that between adsorbate and adsorbent molecules to calculate the isosteric heats. However, this research work focuses more on q_{st}^0 at zero coverage surfaces. Therefore, the Henry’s law constant is employed in the pressure-temperature-uptake co-ordinate system (Clausius-Clapeyron equation) for the calculation of q_{st}^0 . At zero surface coverage, the density of the adsorbed adsorbate molecules in the simulation box is relatively low, which allows the negligible adsorbate-adsorbate interactions.

3.3.1 Molecular Model of Lattice Surface

In physisorption, the interactions between adsorbed species and the adsorbent surface occurs due to weak van der Waals and electrostatic-multipole forces. The total interaction potential is fairly low (≤ 0.5 eV). A single component adsorbate molecule physisorbed on a graphite plane is considered for simplicity. Figure 3.1 shows the geometrical characteristics of a H_2O molecule adsorbed on the hexagonal graphite surface, which contains three particular orientation sites namely the hexagonal centre, C-C bond and carbon atoms. The selected simulation box comprises 10 layers of carbon atoms and each layer includes 41×41 carbon atoms. The sampling adsorbate molecule can move freely. For a given set of carbon atoms r_j , the Lennard-Jones, electrostatic and induction potentials are only functions of adsorbent molecule position vector $\mathbf{r}$ or (X, Y, Z) in graphite co-ordinate system. The carbon atom layers are in X - Y plane with fixed Z , the direction of adsorbate molecule to the honey-comb lattice of graphite. The total interaction potential (U) depends on the relative position of adsorbate molecule to the hexagonal unit cell of graphite. With fixed X and Y , the total interaction potential depends on the Z direction.

Figure 3.1 The simulation model of graphite and water molecule (here H_2O is considered as an example of polar molecule). The edge length of the hexagon of carbon atoms is $d = 1.421 \text{ \AA}$ and the distance of two layers is $l = 3.354 \text{ \AA}$. The position vector points from the i^{th} carbon to the j^{th} atom of the adsorbate molecule. Position vector in adsorbate molecule coordinate system $X'Y'Z'$ can be converted to graphite coordinate system XYZ with a specific rotational matrix and translational vector.

Interaction Potential of Lattice Surface and Adsorbate Molecules

Combining the L-J, electrostatic and induction potentials, the total interaction potential (U_{mM}) term is used to obtain a more complete description of interaction potential for polar molecules, i.e., $U_{mM} = U_{LJ} + U_E + U_I$. The modified L-J potential model is given by [80]

$$U_{LJ}(\mathbf{r}_i - \mathbf{r}_j) = 4\varepsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{|\mathbf{r}_i - \mathbf{r}_j|} \right)^{12} \left[1 + \gamma_R \left(1 - \frac{6}{5} \cos^2 \theta \right) \right] - \left(\frac{\sigma_{ij}}{|\mathbf{r}_i - \mathbf{r}_j|} \right)^6 \left[1 + \gamma_A \left(1 - \frac{3}{2} \cos^2 \theta \right) \right] \right\}, \quad (3.1)$$

where $\mathbf{r}_i$ indicates the position vector of i th adsorbate molecule atom, $\mathbf{r}_j$ is the position vector of the j th carbon atom, ε_{ij} and σ_{ij} are pair well depth potential and collision diameter, γ_R and γ_A are coefficients for repulsion and dispersion component of L-J potential, θ is the angle between position vector $(\mathbf{r}_i - \mathbf{r}_j)$ and outer normal vector of carbon atom plane. According to the Lorentz-Berthelot combining rules, $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$ and $\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$. Equation (3.1) also captures the anisotropic behaviours of graphite. The carbon atom possesses quadrupole polarisability [106] while the dipole moment effects cannot be neglected for polar molecules such as water. The interaction potential of polar molecules with graphite adsorbent consists of charge-charge as well as high-order interactions according to the energy expansion equation [107]. Therefore, the necessity for high-order effects such as dipole-dipole, dipole-quadrupole and induction in polar molecule adsorption is palpable. In the two-body interaction, the polarisation arises from the electric field formed by the opposite source. The strength of the polarisation is characterized by the dipole and quadrupole moment polarisability tensor. Similarly, the transient induced dipole moment is excited by the opposing electric field to a permanent dipole moment. The electrostatic potential between water molecule and carbon atom as shown in Figure 3.2 is derived from the interaction between polar molecule, e.g., water dipolar moment $\boldsymbol{\mu}$ and quadrupole moment $\boldsymbol{\Theta}$ in the electric field $\mathbf{E}(\mathbf{r} - \mathbf{r}_j)$ exerted by the carbon atom.

$$U_E(\mathbf{r} - \mathbf{r}_j) = \boldsymbol{\mu} \cdot \mathbf{E}(\mathbf{r} - \mathbf{r}_j) + \frac{1}{3} \boldsymbol{\Theta} : \nabla \mathbf{E}(\mathbf{r} - \mathbf{r}_j) \quad (3.2)$$

where $\mathbf{r}$ is the position vector for the mass centre of water molecule, $\mathbf{r}_j$ is the position vector of j th carbon atom. The first term of the right hand side indicates the dipolar component of electrostatic potential, which is the inner product of dipolar moment vector $\boldsymbol{\mu}$ and the exerted

electric field $\mathbf{E}(\mathbf{r} - \mathbf{r}_j)$. The second term of the right hand side is quadrupolar, and this is the double-dot product of quadrupolar moment tensor Θ and the electric field gradient (EFG) tensor $\nabla\mathbf{E}(\mathbf{r} - \mathbf{r}_j)$. A screening factor, which is 1 for first layer of carbon atoms and $2/(2.8+1)$ for the rest layers, is applied to the electrical potential of the dipole and quadrupole moment [42].

Figure 3.2 Electrostatic model of water and graphite. Here the dipole moment vector (μ) for water and quadrupole moment matrix (Θ) for water and carbon are shown. $\mathbf{r}_{ij}$ is the position vector from the i th carbon atom to the j th atom of water molecule and $\mathbf{r}_{ij} = -\mathbf{r}_{ji}$. The positive charge for hydrogen atom is q_H and the negative charge of oxygen atom is $-2q_H$. The electric

field generated by the quadrupole moment of carbon atom at position $\mathbf{r}_{ij}$ is $E\theta_C(\mathbf{r}_{ij})$ and the electric field generated by the dipole and quadrupole moment of water is $E\mu_{H_2O}\theta_{H_2O}(\mathbf{r}_{ij})$ and θ_{H_2O} are the quadrupole moment of carbon and water. μ_{H_2O} and $\mu_{H_2O}^I$ are the permanent and transient induced dipole moment of water.

The interaction between transient dipole and permanent charge contributes to the interaction potential, and is represented by

$$U_I(\mathbf{r} - \mathbf{r}_j) = -\frac{1}{2}\boldsymbol{\mu}_p^I \cdot \mathbf{E}_p(\mathbf{r} - \mathbf{r}_j) - \frac{1}{2}\boldsymbol{\mu}_C^I \cdot \mathbf{E}_C(\mathbf{r} - \mathbf{r}_j) \quad (3.3)$$

where $\mathbf{r}$ is the position vector for the mass centre of water molecule, $\mathbf{r}_j$ is the position vector of the j th carbon atom, $\boldsymbol{\mu}_p^I$ and $\boldsymbol{\mu}_C^I$ are the induced dipole moment of polar molecule and carbon that can be calculated according to their polarizability, $\mathbf{E}_p(\mathbf{r} - \mathbf{r}_j)$ and $\mathbf{E}_C(\mathbf{r} - \mathbf{r}_j)$ are the total electric fields of polar molecule and carbon atom due to both permanent and transient induced dipole.

From the geometrical and potential model, the interaction potential $U(z)$ of one adsorbate molecule with the distance z above the surface of adsorbent can be determined. The parallel slit model is shown in Figure 3.3. By definition, the external well potential as a function of z can be expressed with respect to the total interaction potential, which is given by

$$V_{\text{ext}}(z) = U_{\text{mM}}(z) + U_{\text{mM}}(H - z) \quad (3.4)$$

where $H-z$ is the distance of adsorbate molecule to the surface of opposite wall, $H = (H_c - \sigma_{ss})$ is the required distance for adsorbent-adsorbate interactions along z direction, H_c is the maximum possible distance between centres of graphite on opposing wall and σ_{ss} is the size of carbon atom.

Figure 3.3 The parallel slit shape pore model for graphite. The distance of the centre of adsorbate molecule to the surface of multi-layer graphite atoms and the opposing wall are z and $H-z$ respectively for the pore width of H . The external wall potential of the adsorbate molecule in the pore is the sum of the interaction potentials with both walls.

3.3.2 Molecular Model of Amorphous SiO_2 Surface and Water Molecules

The model of amorphous silica is the fundamental problem of this research work. Meanwhile, the adsorbent-adsorbate pair interaction potential is required for the computation of isosteric heat of adsorption. Based on the model of silica gel molecular structure and interaction potential, the isosteric heat of adsorption for silica gel and water is determined by applying the Steele's model [105]. For water molecule in TIP3P water model [108], the hydrogen-oxygen-hydrogen angle is 104.5° and the hydrogen-oxygen bond length is $0.95728 \text{ \AA}$ with partial charge of $+0.4238 e$ and $-0.8476 e$ for hydrogen and oxygen atoms, respectively.

The structure of amorphous silica is considered in this study for simulating and understanding its realistic geometry. Generally, the $\text{Si}(\text{O}_{1/2})_4$ unit is modelled as a tetrahedron with oxygen atoms at the edge and one silicon atom at the centre. At the connection point of the two tetrahedrons, each oxygen atom is shared by two silicon atoms. The amorphicity of the silica structure refers to the uncertainty of the number of silicon atoms in the ring of connected tetrahedrons because the ring can be consisted of 3 to 8 silicon atoms [84].

To generate an amorphous silica network for simulation purposes, the Reverse Monte Carlo (RMC) method is chosen. Hence, we start our analysis with partial radial distribution function as given by [100].

$$g_{uv}(r) = \frac{n_{uv}(r)}{4\rho_v\pi r^2 dr} , \quad (3.5)$$

where $n_{uv}(r)$ is the average number of v atom from u atom between distances of $r - dr/2$ and $r + dr/2$, ρ_v is the mean number density of v atom, r is the distance between atoms, dr is a small distance as compared with r .

The Total Radial Distribution is given by,

$$G(r) = 4\pi r \rho_0 \left[\sum_{u=1, v=u}^m [w_{uv} g_{uv}(r)] - 1 \right] , \quad (3.6)$$

where ρ_0 is total number density of all atoms, and m is the type of all atoms. Take silica for example, $m = 2$ for silica as there are two types of atom in silica structure, i.e., Si and O atoms.

The weighting factor w_{uv} is defined as,

$$w_{uv} = \left(\sum_{k=1}^m c_k \bar{b}_k \right)^{-2} c_u c_v \bar{b}_u \bar{b}_v , \quad (3.7)$$

where $c_u = \rho_u/\rho_0$ is the molar fractions of atom u , and $\bar{b}_u$ is the average bound coherent scattering length. Employing experimentally measured X-ray diffraction data in RMC simulation, $\bar{b}_u$ is replaced by the atomic form factor f_u as shown in Table 3.1

Table 3.1 Average bound coherent scattering lengths and atomic form factor for Si, and O

Atom	Si	O
$\bar{b}$	4.1491	5.803
f	14.41	8.144

The Structure Factor $S(Q)$ is given by,

$$S(Q) = 1 + \frac{1}{Q} \int_0^\infty G(r) \sin(Qr) dr \quad (3.8)$$

The momentum transfer Q is given by,

$$Q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right), \quad (3.9)$$

where λ is the wavelength and 2θ is the diffraction angle.

The structure factor is then used in the chi-square test to determine the acceptance or rejection of one move in RMC simulation and the chi-square test formulation is given by,

$$\chi_S^2 = \sum_{i=1}^N \frac{[S^c(Q_i) - S^e(Q_i)]^2}{\sigma_s^2}, \quad (3.10)$$

where σ_s is the standard error of experimental data, $S^e(Q_i)$ is the structure factor for experimental data and $S^c(Q_i)$ defines the simulated structure factor of the molecular structure after current trial move at the i^{th} given momentum transfer Q_i , and N is the total number of momentum transfer.

Since the purpose of RMC is to construct the adsorbent molecular structure with the knowledge of structure factor that is calculated from X-ray diffraction data of a reference structure, it is necessary to accept trial moves that narrow the gap of characteristic indicator between current and reference structure. The Boolean flag "*IsMoveAccepted*" for accepting or rejecting the trial move based on the chi-square value of previous and current move is given by,

$$IsMoveAccepted = \begin{cases} \text{True,} & \chi_{S,new}^2 < \chi_{S,old}^2 \\ \text{True,} & \chi_{S,new}^2 > \chi_{S,old}^2 \text{ and } e^{-(\chi_{S,new}^2 - \chi_{S,old}^2)/2} > \chi_{DOF,0.05}^2 \\ \text{False,} & \text{else} \end{cases} \quad (3.11)$$

By randomly moving one atom, a new χ_S^2 is calculated, and the move is accepted when $\chi_{S,new}^2 < \chi_{S,old}^2$ or with a probability of $e^{-(\chi_{S,new}^2 - \chi_{S,old}^2)/2}$ when $\chi_{S,new}^2 > \chi_{S,old}^2$.

The total number of stochastic selection and movement of atoms should be as many as possible to ensure that the difference of characteristic indicator between the current and the reference structures is minimised. Meanwhile, the constraint of minimum atom-atom distance is applied to the RMC simulation to reject the move that leads Si-Si, Si-O and O-O distance to be smaller than the minimum acceptable distance. The minimum atom-atom distances are furnished in Table 3.2

Table 3.2 Minimum atom-atom distance used in the RMC simulation

Pair	Si – Si	Si – O	O – O
Distance (Å)	2.8	1.4	2.3

Employing experimentally measured X-ray diffraction data [109] with the reverse Monte Carlo (RMC) simulation technique, the amorphous silica structure is formed. For simplicity, the RMC simulation comprises 1000 Si and 2000 O atoms [110].

In order to verify the molecular model of silica gel from RMC in the literature [110], a set of crystallographic properties such as bond angle distribution function, radial distribution function and structure factor of the amorphous silica structure are calculated. These results are compared with experimentally measured data.

The total radial distribution in Figure 3.4(a) agrees well with partial radial distribution in Figure 3.4(b), where the first peak occurs at around 1.6 Å and the second peak 2.4 Å. While the Si-O bond length in silicate is found between 1.60 Å and 1.64 Å [87], the second peak reflects the correlation between oxygen atoms on the vertices of those tetrahedral [110].

Figure 3.4 Radial distribution function of the SiO₂ structure: (a) total radial distribution (b) partial radial distribution of Si-Si, Si-O and O-O

The bond angle (O-Si-O and Si-O-Si) distribution function of the silica structure is shown in Figure 3.5. The histogram data is obtained by the sampling angle distribution of the amorphous silica structure with a bin size of 1° between $75^\circ \sim 150^\circ$ for O-Si-O and $105^\circ \sim 180^\circ$ for Si-O-Si. Meanwhile, the probability distribution function (PDF) of the bond angle results is also given as a smoothed function of the histogram. The O-Si-O and Si-O-Si are mainly distributed around the two peaks around $104^\circ \sim 112^\circ$ and $130^\circ \sim 145^\circ$. These results agree well with available simulation results in the literature [111]. The most probable bond angle (MPBA) of Si-O-Si is found to be 146° and that of O-Si-O is obtained to be 109.4° [112].

Figure 3.5 Comparison of O-Si-O and Si-O-Si angle distribution function of the SiO_2 structure

The total structure factor of the amorphous silica is shown in Figure 3.6. The momentum transfer Q ranges from $0 \sim 20 \text{ \AA}^{-1}$, for the calculation of structure factor. The calculated $S(Q)$ results of

the amorphous silica structure from RMC agree well with adapted $S(Q)$ data from experimentally measured $Q[S(Q)-1]$ data by X-Ray Diffraction (XRD) [109].

Figure 3.6 Total structure factor of the amorphous silica structure from RMC and XRD

The generated amorphous silica (SiO_2) structure with XYZ coordinate system is shown in Figure 3.7, where a water molecule is observed with rotational angles of α , β and γ correspondingly around three axes of the $X'Y'Z'$ system is placed. The position vectors of both water and SiO_2 molecules are described conveniently by coordinates of x , y and z , and transfer matrix with translation and rotation.

Figure 3.7 The simulation model of silica gel and water molecule. The edge length of the simulation box is $a = b = c = 35.7 \text{ \AA}$. The position vector ($\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$) points from the j^{th} atom (Si or O) of adsorbent to the i^{th} atom (H or O) of the water molecule, where $\mathbf{r}_i$ is the position vector of i^{th} atom of water molecule, $\mathbf{r}_j$ is the position vector of j^{th} silicon/oxygen atom. The position vector in water molecule coordinate system $X' Y' Z'$ can be converted to the silica coordinate system $X Y Z$ with a specific rotational matrix and translational vector.

The mathematical modelling for the calculation of the interaction potential and q_{st}^o of silica-water system is shown in Figure 3.8. In this model, the water molecules are placed between two

layers of SiO_2 molecules for simplicity. Here the position vector ($\mathbf{r}_i - \mathbf{r}_j$) of water molecule can vary freely above the top surface of the silica simulated box. The external normal component value z , which is the vertical distance of water molecule to the silica surface, is related to the total interaction potential between water molecule and two surfaces of silica with the maximum pore width of H . The distance between two silica layers is considered as the pore width for simplicity.

Figure 3.8 The model for calculating the average external wall potential as a function of z for SiO_2 -Water system. The distance of the centre of water molecule to the surface of silica and the

opposing wall are z and $H-z$, respectively given the pore width of H . The external wall potential of the adsorbate molecule in the pore is the sum of interaction potential with both walls.

Here the water molecule can move freely, which means $\mathbf{r}_i$ is free. For each Si or O atom of SiO_2 , the position $\mathbf{r}_j$ is defined in the generated amorphous molecular structure by RMC and the pair Lennard-Jones and electrostatic potentials with water molecule are functions of water-Si/O relative position vector $\mathbf{r}_{ij}$.

Interaction Potential of Amorphous SiO_2 Surface and Adsorbate Molecules

For silica and water system, the interaction potential model is obtained by [113],

$$U = U_{\text{LJ}} + U_{\text{E}} \quad (3.12)$$

where U_{LJ} is the Lennard-Jones potential and U_{E} is the electrostatic potential. The Lennard-Jones potential U_{LJ} is determined by the 12-6 potential

$$U_{\text{LJ}}(\mathbf{r}_i - \mathbf{r}_j) = 4\varepsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{|\mathbf{r}_i - \mathbf{r}_j|} \right)^{12} - \left(\frac{\sigma_{ij}}{|\mathbf{r}_i - \mathbf{r}_j|} \right)^6 \right\} \quad (3.13)$$

where $\mathbf{r}_i$ is the position vector of the i^{th} atom of water molecule, $\mathbf{r}_j$ is the position vector of the j^{th} atom of SiO_2 , ε_{ij} and σ_{ij} are pair well depth potential and collision diameter. According to the Lorentz-Berthelot combining rules, $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$ and $\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$.

The model of electrostatic interaction between silica and water is shown in Figure 3.9. For simplicity, we ignore the bonded effect such as the interaction between the water molecule with functional groups such as hydroxyl group on the surface of silica. The electrostatic interaction between water and SiO_2 comprises equal and opposite charges (q_{H} for water and q_{Si} , q_{O} for SiO_2 molecule) with the separation of $\mathbf{r}_{ij}$

Figure 3.9 Electrostatic interaction between SiO_2 and H_2O molecules. The i^{th} atom of SiO_2 molecule with the electrical charge of q_{Si} or q_{O} interacts with the j^{th} atom of H_2O molecule with the electrical charge of q_{H} or q_{O} . The position vector $\mathbf{r}_{ij}$ characterises the distance between the interaction pair.

The electrostatic potential U_E of charge-charge interaction is given by

$$U_E(\mathbf{r}_i - \mathbf{r}_j) = \frac{q_i q_j}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \quad (3.14)$$

where q_i is the charge of i^{th} atom of the adsorbate molecule, q_j is the charge of the j^{th} atom of silica, ϵ_0 is the vacuum permittivity and r is the charge-charge distance.

Hence, the total interaction potential depends on the orientation and relative position of the water molecule. Furthermore, with fixed orientation, x and y, the total interaction potential which depends only on z is given by,

$$U = \sum_{i=1, j=1}^{A,B} U_{LJ}(\mathbf{r}_i - \mathbf{r}_j) + U_E(\mathbf{r}_i - \mathbf{r}_j) = \sum_{i=1, j=1}^{A,B} [U_{LJ}(z) + U_E(z)]_{\alpha_0, \beta_0, \gamma_0, x_0, y_0} = U(z) \quad (3.15)$$

where A and B are the total number of atoms in water and SiO₂ molecules, $\alpha_0, \beta_0, \gamma_0, x_0$ and y_0 are the fixed rotational angles and positions.

Similar to Equation (3.4), the total interaction potential V_{ext} is the summation of water molecule interactions with both adsorbent walls with the distance of z and H-z, which is expressed by the following equation [13, 114]

$$V_{\text{ext}}(z) = U(z) + U(H - z) \quad (3.16)$$

3.3.3 Molecular Model of Framework Structure and Water Molecules

It is well known that (i) AQSOA-Z01 is a ferroaluminophosphate (FAPO-5) based zeotype with AFI structure, (ii) AQSOA-Z05 is an aluminophosphate (APO-5) based zeotype with AFI structure and (iii) AQSOA-Z02 is based on the silicoaluminophosphate (SAPO-34) zeotype with CHA structure[115-117]. The composition of AQSOA-Z01 [60] is $\text{Fe}_x\text{Al}_y\text{P}_z\text{O}_2 \cdot n\text{H}_2\text{O}$, $x = 0.02-0.10$, $y = 0.35-0.5$, $z = 0.4-0.6$, $n = 0-1$. The sharp peaks of X-ray diffraction (XRD) indicate good crystallinity of both AQSOA-Z01 and AQSOA-Z02 with chemical formulae of $\text{FeAl}_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and $\text{Al}_{0.56}\text{Si}_{0.02}\text{P}_{0.42}\text{O}_2$, respectively [18].

The molecular structure for CHA framework types such as AQSOA-Z02 zeolite is shown in Figure 3.10 (a). On the other hand, the molecular structure for AFI framework types such as AQSOA-Z01/Z05 zeolite is shown in Figure 3.10 (b).

Figure 3.10 The interactions of water molecule with (a) CHA type and (b) AFI type zeolites according to cylindrical pore model. Hence 1, 2, 3 and 4 indicate the layers of cylindrical

channels; C is the center of the channels, r is the distance of one water molecule from the center C.

It is well known that AFI zeolite frameworks such as AQSOA-Z01 and Z05 are ferroaluminophosphate (FAPO-5) and aluminophosphate (APO-5) based zeotypes. Therefore, a molecular structure of Al, P and O atoms is applied to calculate the interaction potentials of water - AFI zeolite systems. On the other hand, the CHA type zeolite such as AQSOA-Z02 silico-alumino-phosphate (SAPO-34) zeotype, and a molecular structure of Si and O atoms is applied in the calculation of interaction potentials between water – CHA zeolite system. For modelling and simulation purposes, the location of water molecules adsorbed in CHA and AFI zeolite frameworks are shown in Figure 3.10 (a) and (b). For simplicity, the interactions between water molecule and zeolite framework are calculated by considering multiple layers of cylindrical channels in CHA and AFI zeolite. For CHA zeolite, the radius for four layers of channel is 3.65 Å, 5.9 Å, 8.75 Å and 10.88 Å. For AFI zeolite (Figure 1b), the radius of four layers of channel is 5.64 Å, 7.24 Å, 8.39 Å and 9.69 Å. As can be observed from Figure 1 (both CHA and AFI cases), R_{CHA} is the radius of the most inner layer (i.e. 1st Layer) of channel and r is the distance of the water molecule to the center of the channel. This means that the water molecule is closer to the surface of the most inner layer of channel as r/R_{CHA} (i.e. r/R) increases.

Interaction Potential of Framework Structure and Adsorbate Molecules

For the zeolite and water system, the 12-6 Lennard-Jones interaction potentials between simulated pairs are applied in the identification favourable adsorptive sites that with larger interaction potential on the surface of zeolites. The sum of pair-wise additive interaction potential is varied with the relative position of water molecule on the surface of zeolite framework and is given by,

$$U_{LJ}(\mathbf{r}_o) = \sum_{i=1}^N 4\varepsilon_{i,o} \left[\left(\frac{\sigma_{i,o}}{|\mathbf{r}_o - \mathbf{r}_i|} \right)^{12} - \left(\frac{\sigma_{i,o}}{|\mathbf{r}_o - \mathbf{r}_i|} \right)^6 \right] \quad (3.17)$$

where $\mathbf{r}_o$ is the position vector of oxygen atom of water molecule, $\mathbf{r}_i$ is the position vector of i th atom of zeolite, N is the number of atoms of zeolite, $\varepsilon_{i,o}$ is the well depth potential of the atom of zeolite with oxygen atom of water molecule and $\sigma_{i,o}$ is the collision diameter.

By varying the position of the water molecule on the surface of zeolite ($\mathbf{r}_o$), the contour plot of potential with fixed z distance and variable (x , y) distance of water molecule is used to identify the favorable adsorptive sites.

The interaction potential of water molecule with a single layer cylindrical channel with radius of R in zeolite framework is given by [118-120],

$$w(r) = \frac{5}{2} \pi \varepsilon_{1s} \left\{ \frac{21}{32} \left(\frac{\sigma_{12}}{R} \right)^{10} \left[\sum_{k=0}^{\infty} \alpha_k \left(\frac{r}{R} \right)^{2k} \right] - \left(\frac{\sigma_{12}}{R} \right)^4 \left[\sum_{k=0}^{\infty} \beta_k \left(\frac{r}{R} \right)^{2k} \right] \right\} \quad (3.18)$$

where r is the radial distance of water molecule to the centre of the channel. The coefficients α_k and β_k are defined by,

$$\alpha_k = \left(\frac{\Gamma(-4.5)}{\Gamma(-4.5 - k)\Gamma(k + 1)} \right)^2 \quad (3.19)$$

$$\beta_k = \left(\frac{\Gamma(-1.5)}{\Gamma(-1.5 - k)\Gamma(k + 1)} \right)^2 \quad (3.20)$$

The gas-solid potential parameter ε_{1s} is given by,

$$\varepsilon_{1s} = \frac{6}{5} \pi \rho_{1s} \varepsilon_{12} \sigma_{12}^2 \quad (3.21)$$

where ρ_{1s} is the atom number density at the surface of cylindrical channel, ε_{12} is the well depth potential of interaction pair and σ_{12} is the collision diameter.

The well depth potentials and collision diameters used in the simulation are shown in Table 3.3. Only the interaction potential between oxygen atom of water molecule and atoms of zeolite framework is considered. These Lennard Jones parameters are from the literature [121-124] while the Lorentz-Berthelot combining rules, $\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$ and $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$ are used in the simulation.

Table 3.3 Well depth potentials and collision diameters of simulated pairs

Zeolite Type	Atom <i>i</i>	Atom <i>j</i>	σ_{ij} (Å)	ε_{ij}/k_B (K)
CHA (SiO ₂)	Si	O	3.49	125.79
	O	O	3.14	48.59
AFI (AlPO ₄)	Al	O	3.58	80.54
	P	O	3.43	120.28
	O	O	3.14	48.59

Another type of interaction potential of water molecule with zeolite framework is described by [105],

$$U_{LJ}(z) = 2\varepsilon_{sf}\rho_s\sigma_{sf}^2\Delta\left[\frac{2}{5}\left(\frac{\sigma_{sf}}{z}\right)^{10} - \left(\frac{\sigma_{sf}}{z}\right)^4 - \frac{\sigma_{sf}^4}{3\Delta(z + 0.61\Delta)^3}\right] \quad (3.22)$$

where σ_{sf} and ε_{sf} are the solid–fluid collision diameter and the solid–fluid well depth potential, respectively. Δ is the separation between the atom planes and ρ_s is the density of the solid. For simplicity, the LJ potential is considered as pair-wise additive and the sum of all the interaction pairs is the total LJ interaction potential.

3.4 Isosteric Heat of Adsorption at Zero Coverage

The average isosteric heat of adsorption is determined on the basis of both the potential function of pore width and the pore structure. Thermodynamic methods to calculate the average isosteric heat of adsorption for both parallel slit and cylindrical shape pores are presented in the following sections.

3.4.1 Isosteric Heat of Adsorption for Parallel Slit Pore

For graphite and polar molecules together with silica and water system, q_{st}^o is calculated using a parallel slit pore model and therefore the interaction of adsorbate molecule with the adsorbent pore is considered as the sum of the interaction of one adsorbate molecule with two opposing surfaces consisting of multi-layer of adsorbent atoms.

Employing the development of Steel [105], the isosteric heat of adsorption at zero surface coverage is $q_{st}^o = -RT^2 \frac{\partial \ln K_H}{\partial T} \Big|_x$, where x is the amount of adsorbate uptake, K_H is the Henry's

law constant and R indicates the ideal gas constant. The Henry's coefficient is given by

$K_H = \frac{1}{A} \left(\frac{Z_1}{kT} \right)$, where A is the adsorbent surface area and $Z_1 = \int_V \exp[-V_{ext}(z)/kT] dz$. V_{ext} is the

total external wall potential and is calculated by equation 3.4. Substituting the values of K_H and Z_1 in the q_{st}^o equation, the average isosteric heat of adsorption as a function of pore width, H , can be calculated as [105, 125],

$$q_{st}^o(H) = RT - N_A \bar{V}_{ext}(z) = RT - N_A \frac{\int_0^H V_{ext}(z) e^{\left(-\frac{V_{ext}(z)}{k_B T}\right)} dz}{\int_0^H e^{\left(-\frac{V_{ext}(z)}{k_B T}\right)} dz} \quad (3.23)$$

Here R is the ideal gas constant, T is the adsorption temperature, N_A is the Avogadro number and k_B is the Boltzmann constant.

q_{st}^o is the separate contributions from (i) thermal energy, and (ii) adsorbate – graphite basal plane/amorphous silica surface interactions. Hence the adsorbate-adsorbate interactions are not considered due to low densities of adsorbate molecules in the Henry's region. It should be noted here that with the fixed distance, z , varying from adsorbate molecule to honeycomb carbon lattice, the total interaction potential depends on the relative position, X and Y , of adsorbate molecule to the hexagonal unit cell of graphite as shown in Figure 3.1.

3.4.2 Isosteric Heat of Adsorption for Cylindrical Pore

For zeolite and water system, the Boltzmann weighted average potential is given by

$$\bar{w} = \frac{\int_0^R \left(w(r) e^{-\frac{w(r)}{k_B T}} \right) r \, dr}{\int_0^R \left(e^{-\frac{w(r)}{k_B T}} - 1 \right) r \, dr} \quad (3.24)$$

where R is the radius of the cylindrical pore, $w(r)$ is the interaction potential as a function of distance r of adsorbent molecule to the centre of the cylindrical pore, k_B is the Boltzmann constant and T is the temperature.

Therefore, the isosteric heat of adsorption is then given by

$$q_{st}^o = RT - N_A \bar{w} \quad (3.25)$$

where R is the universal gas constant and N_A is the Avogadro number.

3.5 Summary

In this chapter, the molecular and pore models of adsorbates with lattice, amorphous surfaces and framework structure are constructed and described. The interaction potential due to adsorbate adsorbent interactions is defined as a function of pore width. Therefore, the isosteric heat of adsorption of three different types of pore structure is connected to the pore width. This new knowledge can be further used in the performance evaluation of adsorption assisted cooling or

desalination cycle based systems. Employing the formulations as presented in this chapter, we can calculate the interaction potentials and the isosteric heat at zero coverage for activated carbon + CO₂, water, silica gel (SiO₂) + water and CHA and AFI types zeolites + water systems as these pairs are generally used for cooling and desalination purposes. The simulation results are presented in the next chapter.

Chapter 4 Simulation Results of Isostatic Heat of Adsorption at

Zero Coverage

4.1 Introduction

The isosteric heat at zero coverage is due to the contributions from (i) thermal energy, and (ii) adsorbate – adsorbent (e.g. graphite basal plane, amorphous silica, zeolite frameworks etc.) surface interactions. In simulation procedures, the adsorbate-adsorbate interactions are not considered due to low the densities of adsorbate molecules in the Henry's region. It should be noted here that with the distance varying from adsorbate molecule to the adsorbent surface, the total interaction potential depends on the relative position of the adsorbate molecules. For hydrogen and oxygen atoms, the partial charges are 0.4238 and -0.8476 elementary charge. On the other hand, the hydrogen-oxygen-hydrogen angle is 104.5° and hydrogen-oxygen bond length is $0.95728 \text{ \AA}$ for water molecule in TIP3P water model [108], which yields both non-zero dipolar and quadrupolar moments. For various adsorbate molecules and carbon atoms, the potential, collision diameter and anisotropy parameters for calculating L-J potential are listed in Table 4.1 [42, 80, 106, 126-128], and the dipole moment, polarisability of dipole and quadrupole moment for calculating electrostatic potential are listed in Table 4.2 [129-131].

Table 4.1 Simulation parameters for calculating Lennard-Jones potential

Atom Pair	$\varepsilon(\text{meV})$	$\sigma(\text{\AA})$	γ_A	γ_R
C-H	2.265	2.965	0.4	-0.54
C-C	2.981	3.305	0.4	-1.05
C-N	2.811	3.390	0.4	-1.05
C-O	3.450	3.141	0.4	-1.05

Table 4.2 Simulation parameters for calculating electrostatic potential

Molecule	$\mu(\text{D})$	α_{xx}	α_{yy}	α_{zz}	$\theta_{xx}(\text{\AA})$	$\theta_{yy}(\text{\AA})$	$\theta_{zz}(\text{\AA})$
Carbon	-	$1.44\text{\AA}^3$	$1.44\text{\AA}^3$	$0.41\text{\AA}^3$	-0.5	-0.5	1
Water	1.855	$1.53\text{\AA}^3$	$1.42\text{\AA}^3$	$1.47\text{\AA}^3$	2.63	-2.50	-0.13
Methanol	1.69	$3.69\text{\AA}^3$	$3.25\text{\AA}^3$	$3.06\text{\AA}^3$	-	-	-
Ethanol	1.69	30.37Bohr^3	33.61Bohr^3	38.87Bohr^3	-	-	-

*For polarizability, $1\text{\AA}^3 = 1.11265 \times 10^{-40} \text{ C} \cdot \text{m}^2/\text{V}$, $1\text{Bohr}^3 = 1.648773 \times 10^{-41} \text{ C} \cdot \text{m}^2/\text{V}$

4.2 Results of Interaction Potentials

4.2.1 Interaction Potential of Graphite with Polar Molecules

The interactions between the graphite and water are presented with respect to five different orientations of water molecules and these are shown in Figure 4.1. Note that the O-C distances are not important here as Figure 4.1 aims to describe five orientations rather than distance between graphite and the water molecule. In fact, the molecule-graphite distance (z) of the five orientations can be varied from 2 to 10 $\text{\AA}$ for the calculation of interaction potential.

For water molecule at orientation 1, the oxygen atom is at the origin and one hydrogen atom is at X axis while the H-O-H is found in XY plane. The oxygen-graphite distance is 3 $\text{\AA}$. For water molecule at Orientation 2, the oxygen atom is observed at the origin. Here one of the hydrogen atoms is at X axis and the other follows toward the graphite surface while the H-O-H plane is found at XZ plane. The oxygen-graphite distance is calculated as 3.5 $\text{\AA}$. The oxygen atom is at the origin for orientation 3, where one hydrogen atom is at X axis, the other hydrogen atom is away from the graphite and the H-O-H orientation is at XZ plane. The oxygen-graphite distance is found to be 3 $\text{\AA}$. The orientation 4 of water molecule is also shown in Figure 4.1, where the oxygen atom is at the origin, both of the hydrogen atoms are pointed away from the graphite, and the angle between H-O bond and X axis is $\frac{180^\circ - 104.52^\circ}{2} = 37.74^\circ$. The H-O-H orientation is

observed with respect to XZ plane. The oxygen-graphite distance is 3 Å. For the water molecule at fifth orientation, the oxygen atom is at the origin. Both of the hydrogens atoms are pointed towards the graphite surface and the angle between H-O bond and X axis is $\frac{180^\circ - 104.52^\circ}{2} = 37.74^\circ$. The H-O-H plane is parallel to the XZ plane. The oxygen-graphite distance is 3 Å.

Figure 4.1 Five different orientations of a water molecule on the graphite surface at the distance of z in Z direction

The interaction energy of a water molecule with the graphite surface as a function of $O \cdots C$ separations (z) for five selected water orientations is shown in Figure 4.2

Figure 4.2 Interaction energy of a water molecule with the graphite surface as a function of C...O separation (z) for five different orientations.

It is clearly observed that the minimum H...C potential is overlapped with the repulsive portion of the O...C potential, and this overlap makes the linear C...H – O configuration most favourable. Any deviation from linearity increases the overlap and makes C...H – O configuration more repulsive. It is found that the interaction potentials of orientations 1, 3, 4 and 5 are larger than those of orientation 2. From orientations 2 and 5, it is found that one or two hydrogen atoms of water molecule are pointed towards the basal plane of graphite, i.e., H atoms are closer to carbon atoms at the same O...C distance. For also orientations 2 and 5, the smaller interaction potential can be explained by the dramatically increased positive repulsion in Lenard-Jones potential added to the total negative potential as the distance (z) between the pair is decreased. The potential energy with respect to maximum well depth ranges from -116 meV to -160 meV depending on the various orientations of water molecule, which agrees well with the available

experimental value of -156 meV[132] as well as calculated value -149 meV reported by Markovic et al. [133] and -126 meV reported by Lin et al. [134] for water adsorption on graphene at zero surface coverage. It is also found that the electrostatic as well as induction potential increases faster when the separation distance (z) is smaller than 3 Å (for water). The calculated potential energy surfaces for the water molecule with various orientations are explained in the Appendix A.

Figure 4.3 shows three different orientations of one methanol molecule on graphite surface at the beginning of adsorption. Here the carbon and oxygen bond is almost parallel to the carbon-carbon bond of graphite or the basal panel (XY plane) as observed in orientation 1. The $\text{CH}_3\text{-OH}$ molecule is rotated 90° with respect to X-axis (orientation 2). On the other hand, the methanol molecule is rotated -90° above the graphite surface (orientation 3).

Figure 4.3 Three different orientations of a methanol molecule on the graphite surface at the distance of z in Z direction

A plot of binding interactions between one methanol molecule and graphite surface is shown in Figure 4.4 for three different $\text{CH}_3\text{-OH}$ orientations. The maximum potential well depth, U_{mM} , of $(\text{CH}_3\text{-OH}\cdots\text{C})$ varies from -210 meV to -180 meV when the methanol molecule is rotated from 0 to 90° along the X-axis. On the other hand, the U_{mM} of $(\text{CH}_3\text{-OH}\cdots\text{C})$ ranges from -210 meV to -170 meV for the rotational angle of methanol varying from 0 to -90° along its X-axis. The

induction potential increases exponentially for the separation distance decreasing from 3 Å to 0. However the electrostatic potential is very small (close to zero, see Appendix A).

Figure 4.4 Interaction energy of a methanol molecule with the graphite surface as a function of $C\cdots CH_3OH$ separation (z) for five different orientations

Figure 4.5 also shows three different orientations of ethanol molecule on a graphite surface. In the orientation 1 of ethanol molecule, both carbon-carbon and carbon-oxygen bonds are almost parallel to the carbon-carbon bond of graphite above the XY plane. From simulation results, it is found that the maximum potential well depth $V_{ext}(C\cdots CH_3-CH_2-OH)$ varies from -300 meV to -270 meV for the rotational angle of ethanol varying from -90° to 90° with respect to its X-axis.

Figure 4.5 Three different orientations of an ethanol molecule on the graphite surface at the distance of z in Z direction

The interaction potential as a function of z is shown in Figure 4.6. It should be noted here that the induction potential increases exponentially for the separation distance (z) decreasing from 3 Å to 0. However the electrostatic potential remains constant with very small values (close to zero, see Appendix A).

Figure 4.6 Interaction energy of an ethanol molecule with the graphite surface as a function of $C \cdots CH_3CH_2OH$ separation (z) for five different orientation

Figure 4.7 shows the maximum interactions for (a) orientation 1 of water molecule (total -167.75 meV = -153.15 meV L-J – 14.61 meV induction + 0.16 meV electrostatic at 2.9 Å), (b) orientation 2 of methanol molecule (total -249.36 meV = -243.15 meV L-J – 6.17 meV induction – 0.032 meV electrostatic) and (c) orientation 3 of ethanol (total -356.43 meV = -348.78 meV L-J – 7.09 meV induction – 0.557 meV electrostatic). On the other hand, the electrostatic potential is very small as compared to L-J potential and provides attractive or repulsive interactions depending on molecule orientations. In addition, the induction effects are relatively significant between polar and graphite because of the strong polarisability of polar molecule.

Figure 4.7 A detailed analysis on interaction potentials $v(z_0)$ for four polar molecules, where the orientations of H_2O , CH_3OH and $\text{CH}_3\text{CH}_2\text{OH}$ are chosen at their maximum q_{st}^o and z_0 .

4.2.2 Interaction Potential of Silica with Water Molecule

In the study of silica and water system, five orientations of water molecule above the amorphous SiO_2 simulation box are shown in Figure 4.8.

Figure 4.8 Five orientations of water molecule above top surface of amorphous silica

It should be noted here that each orientation and position of water molecule on the surface of silica pore contributes equally to the calculation of isosteric heat of adsorption. However, the average q_{st}^o value can only be obtained by conducting an integration over an infinite set of all possible orientations and positions. Some orientations and positions are chosen to study their effects on both interaction potential and q_{st}^o for identifying some favourable adsorptive sites and orientations of water molecule. For example, various orientations of water molecule are studied to predict the interaction potential between water molecule and graphite[135]. For orientations 1 to 5, the rotation angles α , β and γ of water molecule are varied up to $(0^\circ, 0^\circ, 0^\circ)$, $(-90^\circ, 0^\circ, 0^\circ)$, $(90^\circ, 0^\circ, 0^\circ)$, $(-90^\circ, 37.74^\circ, 0^\circ)$ and $(-90^\circ, 37.74^\circ+180^\circ, 0^\circ)$ while the distance between the

centre of water molecule to the surface of silica is ranged from 2 Å to 20 Å. Specifically, the H-O-H plane of water molecule is in XY plane for orientation 1 and the water molecule are rotated around X axis by -90° and 90° for orientation 2 and 3. For orientation 4, the water molecule is rotated around X axis by -90° and then around Y axis by $\frac{180^\circ - 104.52^\circ}{2} = 37.74^\circ$. For orientation 5, the water molecule is rotated around X axis by -90° and then around Y axis by $180^\circ + 37.4^\circ$, which yields the symmetry of orientation 4 and 5 about XY plane.

Effect of orientation on potential with fixed position: variable α , β , γ and z

In order to investigate the effect of various orientations on the interaction potential between water molecule and silica surface, the interaction potentials of water molecule with five orientations are calculated at the same fixed position where $x=0$ Å and $y=0$ Å while z can vary from around 1.5 Å to 20 Å. The interaction potentials as a function of z for various orientations are shown in Figure 4.9. Two completely different trends of interaction potential are observed. Firstly, the interaction potential of all five orientations increase exponentially when the distance z decrease below maximum potential points and converge zero when z increases. Secondly, regardless of the positive region, there exists a maximum total interaction potential of -0.258 eV, -1.340 eV and -1.342 eV, where the attractive and repulsive force are equal, at 2.419 Å, 2.073 Å and 2.035 Å for orientation 1, 2 and 4 correspondingly. Thirdly, the interaction potential is positive and a monotonic decreasing trend for orientations 3 and 5 is observed, which indicates that the repulsive force is stronger than attractive force. Lastly, the comparison of potential component at $z = 4.0$ Å quantitatively characterizes the attraction and repulsion effect. Since the Lennard-Jones interaction of (Hydrogen...Silica) is usually ignored, the total Lennard-Jones potential remains unchanged here as the (Oxygen...Silica) distance for five orientations are the same when there is only rotation and no translation for the water molecule.

Figure 4.9 Interaction potential of water molecule of five orientations with the amorphous silica structure, where electrostatic potential is found significantly very high compared with LJ potential.

As the total interaction potential is significantly affected by the orientation, it is reasonable to conclude that the orientation will be changed to certain favourable orientations in the process of a water molecule being adsorbed on silica pore. These favorable orientations are determined by local geometrical characteristics of silica structure. Therefore, it is also necessary to identify these favourable adsorptive sites on silica surface.

Effect of position on potential with fixed orientation: variable x and z

For the identification of favourable adsorptive sites with relatively stronger interaction, the contour plot of interaction potential for water molecule of orientation 1 on amorphous silica surface is shown in Figure 4.10 Here the $z = 2.65 \text{ Å}$, which is close to the maximum potential

point. Regardless of the positive potential area, some favourable adsorptive sites with relatively larger interaction potential can be identified such as (i) $x = -11.5 \text{ \AA}$ and $y = -11.5 \text{ \AA}$, (ii) $x = -4 \text{ \AA}$ and $y = 4 \text{ \AA}$ and (iii) $x = 12.5 \text{ \AA}$ and $y = 14.5 \text{ \AA}$.

Figure 4.10 Interaction potential of water molecule in orientation 1 with the amorphous silica structure

In order to illustrate the change of interaction potential with water-silica distance z , the water molecule of orientation 1 at five consecutive positions is further studied. Five positions are

chosen in the simulation box due to the fact that the centre ($x = -11.5 \text{ \AA}$ and $y = -11.5 \text{ \AA}$) of Figure 4.10 is a favorable adsorptive site as the interaction potential can be found here.

Employing the concept of interaction potential, a plot of XZ plane ($y = -11.5 \text{ \AA}$) is shown in Figure 4.11. It is found that the interaction potentials of five locations with respect to the x coordinate ($-11 \text{ \AA}$, $-11.25 \text{ \AA}$, $-11.5 \text{ \AA}$, $-11.75 \text{ \AA}$ and $-12 \text{ \AA}$), and the same $y = -11.5 \text{ \AA}$ and $z = 2.65 \text{ \AA}$ vary from around -0.7 eV to -0.75 eV .

Figure 4.11 Illustration of choosing five positions of water in orientation 1 on the amorphous silica structure

The interaction potential of silica and water molecules at the five different positions of water molecules with respect to orientation 1 are shown in Figure 4.12.

Figure 4.12 Interaction potential of water molecule of five positions in orientation 1 with the amorphous silica structure

Hence, the x coordinate varies from -11 Å, -11.25 Å, -11.5 Å, -11.75 Å to -12 Å and y coordinate remains at -11.5 Å, the maximum interaction potential for five different positions are found at -0.782 eV, -0.764 eV, -0.741 eV, -0.712 eV and -0.677 eV at 2.484 Å, 2.592 Å, 2.677 Å, 2.742 Å, 2.787 Å correspondingly.

Effect of position on potential with fixed orientation: variables x, y and z

Even though the sites with positive interaction potential are presented, some favorable adsorptive sites with relatively higher interaction potential are identified from the contour plots of negative interaction potential. These are shown in Figure 4.13.

Figure 4.13 Interaction potential of water molecule at orientation 5 with distance of 2.15 Å, 2.65 Å, 3.15 Å, and 3.65 Å to the amorphous silica structure. The white portion indicates here the positive interaction potential.

The sites with negative interaction potential indicate that the attraction of silica surface to water molecule is stronger than repulsion. Employing the contour plot of interaction potential between water molecule and silica surface at different distances of 2.15 Å, 2.65 Å, 3.15 Å and 3.65 Å, it is found that the interaction potentials at certain favourable adsorptive sites change from negative

to positive with the decrease of distance to silica surface. The interaction potentials at these sites are also decreased rather fast when the distance between water molecule and silica surface is increased. The maximum interaction potential at the most favorable adsorptive site decreases from -1.244 eV, -1.036 eV, -0.855 eV to -0.700 eV when the distance to silica surface increase from 2.15 Å, 2.65 Å, 3.15 Å, to 3.65 Å. This is caused by the exponentially increased Lenard-Jones and electrostatic potential.

4.2.3 Interaction Potential of Zeolites with Water Molecule

The interaction potential of water molecules on CHA type zeolite is shown in Figure 4.14 for the distance of 2.8 Å in z direction.

Figure 4.14 Interaction potential for the adsorption of water molecules on CHA zeolite employing (a) a 3 dimensional, and (b) contour plots.

From Figure 4.14, it is found that the interaction potential is highly negative sides, i.e., provides stronger attraction at certain periodic positions of zeolite framework, which indicates the positions of channels in the zeolite frameworks. Apparently, the water molecules are not adsorbed at those positions with higher interaction potential due to stronger repulsion between

water molecules and zeolite surface. These most favourable adsorptive sites are the possible positions in which the water molecules are adsorbed.

The interaction potential of water molecule on the surface of AFI type zeolite is shown in Figure 4.15 for the distance of 1 Å in the z direction.

Figure 4.15 Interaction potentials of water molecule on AFI zeolite employing (a) a three dimensional, and (b) contour plots.

As compared with CHA type zeolite, the behaviours of periodic positions of interaction potentials as shown in Figure 4.15 are similar to the molecular structure of channels inside the zeolite frameworks, which also indicates that these channels possess the most favourable adsorptive sites for water molecule in the process of adsorption.

The interaction potential of water molecule and the cylindrical channel of CHA zeotype is shown in Figure 4.16.

Figure 4.16 The interaction potential of a water molecule with the cylindrical channel inside CHA zeolite as a function of distance to the centre of the channel.

For CHA zeolite, it is found that the interaction potential is much negatively higher (stronger attraction) at the center of zeolite channel. Apparently, the water molecule will most probably not be adsorbed at those positions with positively higher infarction potential i.e. stronger repulsion to the zeolite surface of the channel. The most favorable adsorptive sites are found at the center of the channel. On the other hand, if multiple layers, other than only the first layer, are considered for interacting with one water molecule, the total interaction potential increases due to the additional interactions of Si and O atoms with water. The interaction potential increases strongly when the second layer is considered. The total potential is not significantly increased even though the effect of third layer is added in the modelling. This is due to the fact that in only O atoms are present in the third layer. The interactions between water molecule and the fourth

layer of the cylindrical channel are very weak. Therefore, the increase in total potential (after addition of fourth layer's effects) is negligible.

The interaction potentials for the adsorption of water molecules on cylindrical channel inside AFI zeotype are shown in Figure 4.17

Figure 4.17 The interaction potential of a water molecule with the cylindrical channel inside AFI zeolite as a function of distance to the centre of the channel

For AFI zeolite, it is found that the maximum negative interaction potential positions are located not at the center of the channel but at r/R of around 0.38. Only O atoms are present in the second layer, and the increase in $w(r)$ is not very high. In case of the third layer, the $w(r)$ increases significantly due to the presence of Al, P and O atoms. The distance from the center to the fourth layer is nearly 10 Å and only oxygen atoms are present in the fourth layer. Therefore, the interactions between water molecule and the fourth layer of the cylindrical channel are very weak.

4.3 Results of Isothermic Heats of Adsorption

4.3.1 Isothermic Heats of Adsorption of Graphite with Water, Methanol and Ethanol

Molecules

Employing the formulation of the previous chapter, plots of q_{st}^0 for different water molecule orientations are shown in Figure 4.18.

Figure 4.18 Isothermic heat of adsorption of single water molecule on graphite lattice at zero surface coverage as a function of z for the selected five H_2O orientations

It is found that the maximum q_{st}^0 of one molecule varies from 0.25 eV to 0.35 eV. For maximum isosteric heat of adsorption, the pore width varies from 2 Å to 4.5 Å with respect to the water molecule orientations. The interaction energy between a water molecule and a single layer of graphite was estimated by Feller and Jordan [136] to be 5.8 ± 0.4 kcal/mol (≈ 0.25 eV). In other reports [137, 138], the q_{st}^0 values at zero surface coverage vary from 1.65 kcal/mol to 4.3 kcal/mol (0.071 eV to 0.185 eV). Employing polarisable potential model, Karapetian and Jordan [139] predicted the heat of adsorption of water molecule and graphite to be 2.50 kcal/mol ($\approx$

0.107 eV). In another study [140], it was found that the water molecule was located at least 3.5 Å above the graphite surface for the maximum q_{st}^o . Not only this, the adsorption energies on graphite surface are varied from 2.90 kcal/mol to 13.72 kcal/mol (≈ 0.125 eV to 0.59 eV) for the distance of oxygen – graphite surface ranging from 3.01 Å to 3.043 Å [134]. These data are also added in Figure 4.18 q_{st}^o is found to be below its liquefaction (0.42 eV) heat due to the hydrophobic behaviour of the graphite surface. It should be noted here that the maximum q_{st}^o is found for the pore width ranging from 2.5 Å to 4 Å, which can be compared with the mean diameter of water molecule (2.9 Å) or the hydrogen bond length of 3 Å.

The plots of q_{st}^o for various orientations of CH₃-OH molecule on graphite surface are shown in Figure 4.19.

Figure 4.19 Isosteric heat of adsorption of single CH₃-OH molecule on graphite lattice at zero surface coverage as a function of z for the selected three CH₃-OH orientations

The higher q_{st}^o at zero CH₃-OH loading varies from 0.35 eV to 0.44 eV due to the combination of methanol-methanol and methanol – graphite interactions with the spill-over of methanol molecules onto the graphite surface. At the beginning of methanol adsorption on carbon pores, q_{st}^o is measured to be 58 kJ/mol ($\approx$ 0.58 eV) at 303 K [43]. For higher pore width, the q_{st}^o decreases due to weak interactions between CH₃OH and graphite surface. As compared with the methanol molecule diameter of 4.2 Å, the maximum q_{st}^o is found for the values of z ranging from 3.4 Å to 4 Å with respect to various methanol molecule orientations. It is also found that at the distance of 3.7 Å, the attractive forces of the more distant groups of alcohol molecules are not compensated by the repulsive forces and the q_{st}^o is measured by Avgul and Keslev [132] to be 10 kcal/mol ($\approx$ 0.43 eV). The adsorption of methanol in graphite pores shows slightly different behaviour as compared to water due to stronger dispersion interactions of CH₃ group with carbon surface. Horikawa et. al. [94] measured the q_{st}^o as 32 kJ/mol ($\approx$ 0.32 eV) for methanol adsorption on graphitised carbon block.

A plot of q_{st}^o for one CH₃CH₂OH molecule is found in Figure 4.20

Figure 4.20 Isosteric heat of adsorption of single ethanol molecule on graphite lattice at zero surface coverage as a function of z for the selected three $\text{CH}_3\text{CH}_2\text{OH}$ orientations

The q_{st}^o values at zero surface coverage varies from 0.56 eV to 0.62 eV for the orientations of ethanol molecule rotating from 90° to -90° . The maximum q_{st}^o is obtained between 3.5 Å and 4 Å as similar to the ethanol molecule diameter of 4.4 Å. At the temperature of 300 K, the simulation results of q_{st}^o at zero surface coverage are found in good agreement with the estimated experimental values that range from 13 ± 0.4 kcal/mol (≈ 0.54 eV) to 16 ± 0.4 kcal/mol (≈ 0.688 eV) given by the reference[141]. From the simulation study, the optimum pore width is found to be 3.5 Å. This is due to the fact that at the distance of 3.5 Å, the attractive forces of isometric alcohol molecules are not compensated by the repulsive forces.

4.3.2 Isosteric Heats of Adsorption of Silica with Water Molecule

The isosteric heat at zero coverage (q_{st}^0) for water adsorption on SiO_2 is calculated as a function of pore width (H). These results are presented in Figure 4.21, with respect to five different positions of water molecule on SiO_2 surface.

Figure 4.21 q_{st}^0 of water of position 1~5 of orientation 1 on amorphous silica

The q_{st}^0 values are increased from 4 Å and the maximum values are found 1.578 eV, 1.542 eV, 1.494 eV, 1.436 eV and 1.368 eV for pore widths of 4.618 Å, 4.836 Å, 5.007 Å, 5.358 Å and 5.223 Å depending on five positions of water molecule. Later, the q_{st}^0 drops rapidly down to the transient region of pore width varying from 8 Å and 13 Å. Between 13 Å and 20 Å, all of the five q_{st}^0 values converge around 50 kJ/mol (≈ 0.52 eV) synchronously. The experimentally measured q_{st} data by Chua et al. are added in Figure 4.21 for comparison purposes. The q_{st} of types RD

and A silica gel are calculated as 2510 kJ/kg (≈ 0.47 eV) and 2710 kJ/kg (≈ 0.51 eV) respectively [142].

The Grand Canonical Monte Carlo (GCMC) simulation is carried out to predict the q_{st}^0 values of amorphous silica structure and water system. The q_{st}^0 for the pore widths of 5 Å and 10 Å at the relative pressure of 0.05 is found to be 1.636 eV and 1.942 eV. It can be found that GCMC simulation result is close to the maximum q_{st}^0 values at pore width of 5 Å but the deviation increases for larger pore width. The isosteric heat of CaCl₂-in-silica gel+ water system at low uptake of 0.05 kg/kg is found to be around 3000 kJ/kg (≈ 0.56 eV)[143]

4.3.3 Isosteric Heats of Adsorption at Zero Coverage for Zeolites with Water Molecule

The simulation results of the isosteric heat at zero coverage employing two types of interaction potential equations are presented here.

With a variable pore size assumption, the simulation results of the isosteric heat at zero coverage for water adsorption on CHA and AFI types zeolite frameworks are employing cylindrical interaction potential equation is shown in Figure 4.22. For simplicity, both of the zeolite frameworks of two zeotypes are considered as layers of T and O atoms (T = Al, P for AFI structure or T= Si for CHA structure) and the total interaction potential is obtained as introduced in Chapter 3.

Figure 4.22 Isosteric heat of adsorption of water on zeolite of CHA and AFI framework type

Employing equations in Chapter 3, the values of q_{st}^0 as a function of pore width are calculated, and these results are shown in Figure 4.22, which considers only the micro-pore ranges ($< 20 \text{ Å}$) and the first layer of CHA and AFI zeolites. The isosteric heats for first layers are found to be (i) 34.22 kJ/mol for CHA (AQSOA-Z02) type zeolite at the pore diameter of 7.3 Å and (ii) 27.37 kJ/mol for AFI (AQSOA-Z01 and Z05) type zeolite at the pore diameter of 11.28 Å. These two values are also shown in Figure 4.22. At multiple layers, the q_{st}^0 values are found higher due to additional interaction potentials of other layers comprising Si and O atoms for CHA type and Al, P and O atoms for AFI type zeolites. For example, up to 4 layers, the isosteric heats for CHA and AFI zeolites are found to be 44.39 kJ/mol and 33.77 kJ/mol, respectively.

4.4 Summary of Chapter 4

4.4.1 Graphite and Water, Methanol and Ethanol Molecules

The interaction potential curves as a function of adsorbate – adsorbent separation distance z and q_{st}^o curves as a function of pore width H illustrate how these molecules interact with a graphite surface. Some important features are as follows:

- (i) The maximum potential well for graphite – water system constitutes 91.28% Lennard Jones potential $v_{LJ}(C\cdots H_2O)$, 8.7% induction potential $v_I(C\cdots H_2O)$ and 0.012% electrostatic $v_E(C\cdots H_2O)$. The maximum potential well depth depends on various orientations of H_2O molecule on graphite structure. The maximum q_{st}^o at zero surface coverage is found to be 0.35 eV at orientation 1, where the oxygen atom is at the origin, one H atom is at the X-axis and H – O – H is obtained in the X-Y plane, and the simulation result is very close to the experimental data of 0.32 eV. For water molecules, the electrostatic contribution for $v(z)$ is very close to zero and provides attractive or repulsive interactions between adsorbate and graphite molecules.
- (ii) For ethanol and methanol, the electrostatic contribution is close to zero and provides both attractive and repulsive interactions. The $v_{LJ}(C\cdots CH_3-OH)$ and $v_{LJ}(C\cdots CH_3-CH_2-OH)$ contributions are more than 90%. The induction interactions are less than 10%. For both methanol and ethanol molecules, the induction potential increases exponentially for the separation distance decreasing from 3 Å to 0. However, the electrostatic potential remains constant and the value is very close to zero.

4.4.2 Amorphous Silica and Water

The structure of amorphous silica is constructed using the Reverse Monte Carlo (RMC) method. The radial and angle distribution functions together with the structure factor of the generated structure is compared with experimentally measured results to verify this molecular model. With

the validated silica structure, the intermolecular potential between water and silica that integrating LJ and electrostatic potential are determined and applied in the calculation of isosteric heat of adsorption at zero surface coverage.

(i) The partial radial distribution and structure factor of the reference silica structure constructed by the Reverse Monte Carlo method are calculated to confirm the validity of SiO_2 structure for q_{st}^o calculation. Furthermore, the bond angle (O-Si-O and Si-O-Si) distribution functions of the silica structure are calculated. The O-Si-O and Si-O-Si angles are mainly around $104^\circ \sim 112^\circ$ and $130^\circ \sim 145^\circ$ and are in good agreement with other simulation results while the most probable bond angle (MPBA) of Si-O-Si is found 146° and that of O-Si-O is 109.4° .

(ii) The interaction potential is also determined by the water-silica distance z according to the interaction potential of five positions in orientation 1, which are chosen in the simulation box due to the fact that the centre $x = -11.5 \text{ \AA}$ and $y = -11.5 \text{ \AA}$ is a favourable adsorptive site due to the presence of the negative interaction potential. While the x coordinate is varied from $-11 \text{ \AA}$ to $-12 \text{ \AA}$ and y coordinate is remained fixed at $-11.5 \text{ \AA}$, the maximum interaction potential ranges from -0.782 eV to -0.677 eV .

4.4.3 Zeolite and Water

The isosteric heat of adsorption for water on three CHA and AFI types zeolites such as AQSOA-Z01, AQSOA-Z02 and AQSOA-Z05 are studied. The following findings are obtained.

(i) The most favourable adsorptive sites with negatively larger potentials are identified at the positions of channels inside the zeolite framework.

(ii) The isosteric heat of adsorption of water adsorption on first layer of CHA and AFI types zeolites are predicted to be 34.22 kJ/mol for CHA (AQSOA-Z02) type zeolite at the pore diameter of $7.3 \text{ \AA}$ and 27.37 kJ/mol for AFI (AQSOA-Z01 and Z05) type zeolite at the pore

diameter of 11.28 Å. At multiple layers, the q_{st}^o values are found higher due to additional interaction potentials of other layers comprising Si and O atoms for CHA type and Al, P and O atoms for AFI type zeolites. For example, up to 4 layers, the isosteric heats for CHA and AFI zeolites are found to be 44.39 kJ/mol and 33.77 kJ/mol, respectively.

The isosteric heat at zero coverage is essential for the calculation of energetic performances of adsorption assisted cooling and desalination. In that case the isotherms data are needed for device simulation purposes. The next chapter will discuss about the experimental study of adsorption isotherms for silica gel + water, various zeolites + water and activated carbon + CO₂, CH₃-OH or CH₃-CH₂-OH systems.

Chapter 5 Measurement of Adsorption Uptakes under Static

Conditions

Evaluation of the amount of water vapour on silica gel and AQSOA-type zeolites for various temperatures and pressures is needed to design an adsorption chiller for air conditioning and desalination applications. On the other hand, the amounts of CO₂ uptakes on activated carbons have to be determined for the design of adsorption refrigeration system. In this chapter, an experimental study for calculating adsorbate uptakes is described.

5.1 Experimental Investigation

5.1.1 Measurement of CO₂ Uptakes on Activated Carbon

The amount of CO₂ uptake was determined by the Control Volume Variable Pressure (CVVP) method as shown schematically in Figure 5.1. The CVVP apparatus consists of three sections, CO₂ storage cylinder, charging and adsorption chambers. The charging section provides a calibrated space for CO₂ to charge into, where the initial mass of CO₂ gas can be measured. The adsorption section offers an adsorption site for the adsorbent + adsorbate pair. The volume of both adsorption and charging sections are calibrated with water and are recorded as V_{rec} and V_{char} , respectively. The charging and adsorption chambers are heated with a hot water bath to ensure the same constant temperature during the whole adsorption process. All the pipes are covered with heating wire and insulation to maintain a target temperature with an adjustable heater in the experiment. The adsorption cell had been designed with a high aspect ratio, so that the adsorbent could be spread on the large flat base. Pressure transducers (type Kyowa-PGS-200KA, uncertainty of 0.2 % full scale) are used to measure the pressures of charging and adsorption cells. The temperature of charging chamber was recorded by class-A Pt 100 Ω RTDs.

with uncertainty of $\pm 0.15^\circ\text{C}$. The temperature of adsorption chamber was controlled by the DT-670B-CU-HT silicon diode thermometers with the uncertainty of $\pm 0.1^\circ\text{C}$.

Figure 5.1 Schematic diagram of CVVP apparatus for measuring CO₂ adsorption of activated carbons.

The pressure within the adsorption chamber was measured by GS4200-USB digital pressure transducer with an error of $\pm 0.1\%$. Before the experiments, the adsorbent sample was dried in an oven at 420 K for 6 h and then placed in the adsorption chamber after calculating its dry mass. The volume occupied by carbon sample within adsorption chamber has been taken into account by helium/argon gas calibration. Both the charging and adsorption cells were evacuated using a rotary vane vacuum pump (Brand: VACUUBRAND, Model: RC 6) for 6 h and the temperature of adsorption cell was kept at 420 K for regeneration. Prior to the first charging of CO₂, the temperature of the charging cell was kept at 298 K, while the adsorption cell temperature was ranged from 298 K to 363 K depending on experimental conditions. A certain amount of CO₂

was then dosed into the charging cell. At the first step of the experiment, there was residue gas inside the adsorption cell and the mass of residue gas was calculated by $m_{rec} = V_{rec}\rho_{rec}$, where V_{rec} is the volume of adsorption cell and ρ_{rec} is the density of residue gas. The adsorbate of charging cell is $m_{char} = V_{char}\rho_{char}$, where V_{char} is the volume of charging cell and ρ_{char} is the density of CO₂ during charging. By turning on and off the “adsorbate gas introducing valve”, a certain amount of CO₂ was dosed into the adsorption cell for adsorption at the desired temperature. The thermal equilibrium was attained within 30 min to 1 hour. All time dependent adsorption data are collected from initial to final states. The residual mass left in the apparatus is $m_{red} = V_{char}\rho'_{char} + V_{rec}\rho'_{rec}$, where ρ'_{char} and ρ'_{rec} is the density of the residual CO₂ in the charging and adsorption cells. Therefore, the subsequent adsorbed mass (m_a) was calculated by the equation: $m_a = m_{rec} + m_{char} - m_{red}$. The amount of adsorbate uptake as a function of pressure and temperature was calculated as $q = m_a/M_s$, where M_s is the mass of dry activated carbons. The CO₂ density was calculated by indexing NIST Standard Reference Database 23 of Version 8.0 [144]. The limitations of the volumetric methods are (i) indirect measurement method, (ii) possibility of high errors (in that case, proper and high quality calibrations are needed), and (iii) time consuming, i.e., proper investigations are required during thermal equilibrium.

5.1.2 Measurement of Water Uptakes on Silica Gels and AQSOA Zeolites

The experimental investigations for water adsorption on zeolites samples were carried out by a thermogravimetric analyser. Figure 5.2 shows the schematic diagram for understanding the measurement of water vapour uptakes at various temperatures and pressures. At first, the zeolite sample was dried in an oven at 160°C for about 2 hours to remove all moisture from the sample. The zeolites were then placed on the sample cell, which was held by a microbalance, located

above the adsorption chamber, known as the balance head. The balance head had to be set at a temperature at least 15°C above the experimental conditions to eliminate the condensation effects in the adsorption chamber. Dry Nitrogen (99.999% purity) was introduced into the adsorption chamber to control buoyancy effects of the balance. The vapour was generated in a humidifier. The temperature inside the humidifier was measured by a class A RTD temperature sensor with an accuracy of ± 0.15 °C. The vapour charging flow rate was controlled automatically. The adsorbent is placed in the quartz sample bowl inside the reaction chamber which has a radiant heater for maintaining a constant temperature. A vacuum pump was used for vacuuming and purging the system before an experiment and maintaining the adsorption chamber pressure in coordination with a vacuum controller.

Figure 5.2 Schematic diagram of the adsorption/desorption isotherm and kinetics setup

During the adsorption experiment, both the pressure and temperature of the adsorption chamber were controlled within acceptable error ranges. Hence, the temperature probes and the humidity sensor were used to calculate the temperature and relative pressure (P/P_s). The humidity probe stabilises the value of P/P_s in the adsorption chamber by controlling the flow rate of dry N_2 . If P/P_s is higher than that of expected values, the flow rates of dry N_2 were increased and the N_2

flow across the humidifier is stopped. The excess water vapour content was purged out of the chamber so that the P/Ps can be obtained at the desired value, which also introduces the right distribution of dry nitrogen to water vapour. If P/Ps was lower, the dry N₂ flow through the humidifier was increased for the addition of water vapour content within the adsorption chamber. The water uptake was measured on the basis of P/Ps and the set temperature of the adsorption chamber. During the adsorption process, the amount of total mass, M_t , was increased due to the addition of water vapour from the humidifier. Subsequently, the M_t of the adsorbent – adsorbate system is further increased as more water vapour is added to the chamber, making M_t a function of pressure. The mass of adsorbate, m_a , at any pressure P_i can be determined by $m_{a,i} = M_t(P_i) - M_t(P_o)$, where i is a variable to signify each pressure point, and $M_t(P_o)$ defines the total mass of zeolite + water vapour at initial known pressure P_o . The mass of adsorbate allows the gravimetric uptake to be calculated by $q_i = m_{a,i}/M_s$ for each pressure point, where M_s is the mass of dry solid adsorbent. The adsorption kinetic data was also achieved while measuring the water uptake of the adsorbent as a function of time. Adsorption kinetic determines the amount of time taken for the adsorption to reach equilibrium at given temperature and pressure. Thus, at a specific temperature and pressure, the change in mass of adsorbent due to the increment of water vapour uptake was measured with respect to time.

For a given temperature, the P/P_s values were varied to attain the water uptakes to form the isotherm. Before achieving the new isotherm data, the adsorbents were retrieved from the adsorption chamber and placed in an oven at 150°C for regeneration. Then, with the regenerated adsorbent placed into the adsorption chamber, the adsorption chamber was purged with dry nitrogen at 65°C. The experiment was repeatedly performed to ensure that the repeatability is within the experimental uncertainties.

5.2 Results and Discussions

5.2.1 CO₂ Adsorption Isotherms

The first two sets of data pertain to the adsorption of CO₂ on pitch based activated carbon (type Maxsorb III) and activated carbon fibre (ACF type A-20) for the temperatures ranging from 303 K to 363 K and pressures up to 10 MPa, and these are shown in Figure 5.3 (a) and (b). The amount of CO₂ uptakes on BPL and Norit activated carbons at 298, 308, 323 and 338 K and pressures up to 600 kPa are observed to be of convex curvature of Type I, as shown in Figure 5.3 (c) and (d). Another set of data pertain to the adsorption of CO₂ on monolith activated carbon. These are shown in Figure 5.3 (e). These experimental data can be predicted by adsorption isotherms equations namely Langmuir, Tóth and Dubinin-Astakhov (D-A). Hence, the Tóth isotherm equation fits well with experimentally measured adsorption isotherm data.

The Tóth isotherm model is presented by

$$q = q^o \frac{KP}{\left\{1 + (KP)^n\right\}^{1/n}} \quad (5.1)$$

where the Henry's constant is expressed as $K = K_o \exp(\frac{q_{st}}{RT})$. Here K_o is the pre-exponential coefficient relating to the entropy of adsorption (ΔS), R is the universal gas constant and q^o indicates the limiting uptake [145]. The limiting uptake, q^o , is related to the adsorbent pore volume. The heterogeneity coefficient n lies in the range 1 to 3 depending on the pore structures of adsorbents [146]. The Tóth isotherm equation can be further expressed as

$$P = \frac{1}{K} \left\{ \frac{(q/q^o)^n}{1 - (q/q^o)^n} \right\}^{\frac{1}{n}}.$$

The isosteric heat of adsorption is written as $q_{st} = RT^2 \frac{\partial \ln P}{\partial T} |_q$. Substituting the values of P in

q_{st} equation, we have $q_{st} = -RT^2 \frac{\partial \ln K}{\partial T}$. The isotherms parameters are presented in Table 5.1

Table 5.1 Adsorption isotherm parameters for various carbonaceous materials and CO₂ system

Adsorbent + CO ₂ system	q_{st} (kJ/mol)	n	q^o (kg/kg)	K_o (kPa ⁻¹)	Pore volume (cm ³ /g)
Maxsorb III + CO ₂	20.37	0.664	3.06	1.17×10^{-7}	1.70
ACF (A-20) + CO ₂	19.23	0.7	1.56	2.55×10^{-7}	1.05
BPL activated carbon + CO ₂	25.00	1.2	0.623 – 0.001 T	1.10×10^{-7}	0.36
Monolith activated carbon + CO ₂	24.02	1.0	0.25	6.20×10^{-7}	0.60
Norit activated carbon + CO ₂	24.8	0.95	0.55	7.50×10^{-8}	0.47

Figure 5.3 Adsorption isotherms diagrams for CO₂ uptakes on (a) Maxsorb III (b) ACF-A20 (c) BPL (d) Norit and (e) honeycomb monolith type activated carbons for the temperatures ranging from 303 K to 373 K

5.2.2 Water Adsorption Isotherms

In the present study, the temperatures and pressures investigated ranged from (303 to 338) K, and from (1 to 7) kPa, respectively. The uncertainty of pressure ranges from (± 10 to 200) Pa. Emphasis is placed on the conditions experienced in the adsorber, since this is the range of conditions that directly determines the cooling capacity.

Adsorption equilibrium data of water vapour on three types of silica gels were obtained. Figure 5.4 (a), (b) and (c) depict the experimental equilibrium data for the type 'RD', 'A' and '3A' silica gels with water vapor, respectively.

The performance of type 'RD' silica gel water system employed by the adsorption chiller manufacturer available in the form of the Henry's isotherm is also superimposed for comparison [147]. The data of the manufacturer have been obtained for temperatures from 328 to 358 K, and for pressures from 1 to 5 kPa. From Figure 5.4, it is found that the isotherms of $T = 304$ K and $T = 310$ K for both type 'RD' and 'A' silica gel-water systems exhibit signs of onset of monolayer saturation at higher pressures. The Tóth's equation is found to fit the experimental data of both type 'RD' type 'A' and type '3A' silica gel-water systems well and is therefore used to find the isotherm parameters and isosteric heats of adsorption. The Toth isotherms parameters are shown in Table 5.2

Table 5.2 Correlation coefficients for the two grades of Fuji Davison silica gel + water systems

(The error quoted refers to the 95% confidence interval of the least square regression of the experimental data)

Type	K_o	q_{st}	q^o	t	Remarks
	(kg/(kg.kPa))	(kJ/kg)	(kg/kg)		
‘A’	$(4.65 \pm 0.9) \cdot 10^{-10}$	$(2.71 \pm 0.1) \cdot 10^3$	0.4	10	By Tóth
‘RD’	$(7.30 \pm 2) \cdot 10^{-10}$	$(2.693 \pm 0.1) \cdot 10^3$	0.45	12	By Tóth
3A	$(7.30 \pm 2) \cdot 10^{-10}$	$(2.622 \pm 0.1) \cdot 10^3$	0.36	8	By Tóth

Figure 5.4 (a): Isotherm data for water vapour onto the type ‘RD’ silica gel; for experimental data points with: (■) $T = 303$ K; (○) $T = 308$ K; (▲) $T = 313$ K; (□) $T = 323$ K; (+) $T = 338$ K, for computed data points with solid lines for the Tóth’s equation.

Figure 5.4 (b): Isotherm data for water vapour onto the type 'A' silica gel; for experimental data points with: (■) $T = 304$ K; (○) $T = 310$ K; (▲) $T = 316$ K; (□) $T = 323$ K; (+) $T = 338$ K, for computed data points with solid lines for the Tóth's equation.

Figure 5.4 (c): Isotherm data for water vapor onto the type '3A' silica gel; for experimental data points with: (■) $T = 304$ K; (○) $T = 308$ K; (*) $T = 313$ K; (▲) $T = 323$ K; (+) $T = 338$ K, for computed data points with solid lines for the Tóth's equation.

Figure 5.5 (a – c) show the experimentally measured data for the adsorption of water vapour on AQSOA-Z01, Z02 and Z05 zeolites under static conditions. The experimental data of Shimooka et al. [116] at 298 K are included here for comparison purposes. From Figure 5.5 (a), the hydrophobic length of AQSOA-Z01 begins from Henry's region to the relative pressure (P/P_s) of 0.1. When P/P_s is higher than 0.1, the water uptake increases sharply. This may be due to the fact that AQSOA-Z01 is mainly fabricated by AlO_4 , PO_4 and FeO_4 tetrahedron, and the Al and P atoms are partially replaced by Fe atoms. The Fe atoms attract more water molecules at higher pressure due to higher enthalpies of adsorption. On the other hand, Figure 5.5 (b) shows that AQSOA Z02 type zeolite has a very short hydrophobic length with water adsorption due to the presence of SiO_4 tetrahedrons. With the presence of SiO_4 in AQSOA-Z02 zeolite structure, water molecules are attracted towards this adsorbent at lower relative pressure as Si atoms has higher affinity with water. Similarly at the higher temperature of 333K, the isotherm also shows a short hydrophobic length at lower relative pressure. By considering the short hydrophobic length at lower pressure AQSOA-Z02 + water system provides S-shape or type V isotherm and indicates the presence of a pore filling phenomena. The isotherms at very low pressures are also shown in Figure 5.5 (b). Figure 5.5 (c) indicates that AQSOA-Z05 has longer hydrophobic length up to the relative pressure of 0.2 due to the absence of both Fe and Si atoms in AQSOA-Z05 structures. The crystal structure of Z05 consists mainly of AlO_4 and PO_4 tetrahedrons only.

Figure 5.5 Experimentally measured water uptakes on (a) AQSOA-Z01, (b) AQSOA-Z02 and (c) AQSOA-Z05 zeolites under static conditions.

Generally, Langmuir, Tóth and Dubinin-Astakhov equations fail to explain the S-shaped isotherm within acceptable error ranges [148]. Firstly, the Langmuir isotherm is derived based on two major assumptions that the adsorbent surface is homogeneous and the adsorptive sites are localized. These assumptions are not true for AQSOA zeolites. From the discussion of section 4.2.3 Interaction Potential of Zeolites with Water Molecule, we know that the most favourable adsorptive sites for water molecule adsorbed on AFI type zeolite are located in the centre of

channels in the structure. Even for CHA type zeolite, the favourable adsorptive sites are located at the surface of the simulated structure. The CHA porous surface is not homogeneous. At low pressure region the water interaction on CHA zeolite is not very strong and shows the hydrophobic behaviours. However at relatively higher pressure regions, the water adsorption interaction is very high and the monolayer it is formed at the saturated pressure. The isotherm curve is not type I. Therefore, the Langmuir isotherm is not suitable for fitting adsorption data for AQSOA zeolite and water. Secondly, both Toth and DA isotherm are empirical equations and are generally valid for heterogeneous surface. Both DA and Toth (modified Langmuir) provide high errors with the experimental data of AQSOA-Zeolites and water systems. The adsorption isotherm model developed by Sun and Chakraborty [34] can almost cover the whole quadrant in a P (pressure)-q (uptake) coordinate system and therefore is adopted in the curve fitting of experimental data to reduce the fitting uncertainties.

$$\theta = \frac{K(P/P_s)^m}{1 + (K-1)(P/P_s)^m} \quad (5.2)$$

where K is the isotherm coefficient and is defined by $K = \alpha \exp[m(q_{st}^o - h_{fg})]$, α is the pre-exponential coefficient, m defines the surface-structural heterogeneity factor, q_{st}^o is the isosteric heat of adsorption at zero surface coverage, h_{fg} indicates the enthalpy of evaporation and R is the gas constant. θ is the surface adsorbate coverage and is given by q/q^o , where q is the amount of water vapour uptake and q^o is the limiting uptake. Hence, $(q_{st}^o - h_{fg})$ resembles the adsorption characteristics energy and can also be approximated from experimental data. Employing the concepts of Lennard – Jones and electrostatic potentials, the isosteric heat of adsorption at zero coverage (q_{st}^o) is calculated as a function of pore width (as described in the previous chapter) or

$$q_{st}^o = RT - N_A \frac{\int_0^H V_{ext}(z) e^{\left(-\frac{V_{ext}(z)}{kT}\right)} dz}{\int_0^H e^{\left(-\frac{V_{ext}(z)}{kT}\right)} dz} \quad (5.3)$$

Hence H_c indicates the pore width and V_{ext} is the adsorbent wall potential as derived by $V_{ext}(z) = U_{sf}(z) + U_{sf}(H - z)$, where H is the distance between the nuclei of the outer adsorbent atoms on opposite walls. The adsorbent-adsorbate interaction potential (U_{sf}) as a function of pore

width direction (z) is defined as $U_{sf} = 2\pi\epsilon_{sf}\rho_s\sigma_{sf}^2\Delta\left[\frac{2}{5}\left(\frac{\sigma_{sf}}{z}\right)^{10} - \left(\frac{\sigma_{sf}}{z}\right)^4 - \frac{\sigma_{sf}^4}{3\Delta(0.61\Delta + z)^3}\right]$,

where σ_{sf} and ϵ_{sf} are the solid-fluid collision diameter and the solid-fluid well depth potential, respectively. Δ defines the separation between the adsorbent planes and ρ_s is the density of solid adsorbent. For water adsorption cases: $\sigma_{sf} = 3.43 \text{ \AA}$, $\epsilon_{sf} = 8.119 \times 10^{-21} \text{ J/mol}$, $\Delta = 3.35 \text{ \AA}$ and $\rho_s = 0.055$.

The experimentally measured water uptakes data are also fitted with Dubinin-Astakhov (DA) and the modified Langmuir equation to represent the characteristics curve. Mathematically, the DA equation is given by [5]

$$q = q^o \exp\left[-\left\{\frac{RT}{E} \ln\left(\frac{P_s}{P}\right)\right\}^n\right] \quad (5.4)$$

where E defines the characteristics energy, R is the gas constant, P_s defines the saturated pressure and n is the number of adsorptive sites or heterogeneity coefficient. The modified Langmuir adsorption isotherm equation is formulated on the basis of Fermi-Dirac distribution function, and it includes the loading, the adsorbent-adsorbate interaction and the surface structural heterogeneity factors [33]

$$q = q^o \beta \left(\frac{P}{\phi^*}\right) / \left[1 + (\beta^{t_1} - \alpha) \left(\frac{P}{\phi^*}\right)^{t_1}\right]^{\frac{1}{t_1}} \quad (5.5)$$

where $\frac{P}{\phi^*} = \left(\frac{P}{P_s}\right) \exp \left\{ \frac{\phi_m}{RT} \left[1 - \left(\frac{P}{P_s}\right)^{n_1} \right] + z \right\}$. Here ϕ_m is the minimum potential energy, β is the

loading factor, t_1 defines the surface heterogeneity, n_1 is the adsorbate-adsorbent interaction factor and z indicates the compressibility factor.

Hence, the experimental data are fitted with the isotherm model of Equation (5.2) to calculate isotherm parameters for AQSOA zeolites + water systems. Figure 5.5 (a) indicates that the isotherm model is closely fitted with the experimental data within 5% error margins both in the Henry and saturated pressure regions. However, the errors are higher than 8% for the relative pressure ranging from 0.1 to 0.3. It is also found from Figure 5.5 (b) that Equation (5.2) shows a better curve-fitting (error within 5%) for AQSOA-Z02 + water system as compared with other isotherms (Equations (5.4) and (5.5)). Figure 5.5 (c) indicates the S-shaped isotherm phenomenon, where the isotherm model of Equation (5.2) provides relatively higher errors (errors > 5%) for the relative pressures varying from 0.1 to 0.3. For water adsorption, the isosteric heat at zero coverage is calculated by Equation (5.3). According to equation (5.2), it should be noted here that α is related to the entropy of adsorption and that m is responsible for the shape of the isotherm curve. From isotherm data, it is found that the hydrophobic length of AQSOA Z01 and Z05 depends on m significantly. Hence the experimentally measured isotherm data are also fitted with Dubinin-Astakhov (DA) and the modified Langmuir equations. Both DA and Langmuir equations are able to handle the experimental data between 298 K and 318 K within experimental uncertainties as these equations are formulated from the rigour of micro-pore filling theory. However, DA and modified Langmuir equations do not work well at higher temperature adsorption. The parameters of DA and the modified Langmuir isotherm equations are also listed in Table 5.3

Table 5.3 Parameters of isotherm equations for various AQSOA zeolites – water systems

Isotherm equation							
System	q ^o (kg /kg)	q _{st} ^o (kJ/kg)		m		α	
AQSOA-Z01 + Water	0.215	3030		4.9		9.0 × 10 ⁻⁷	
AQSOA-Z02 + Water	0.29	4560		1.01		7.0 × 10 ⁻⁶	
AQSOA-Z05 + Water	0.22	2800		6.55		6.77 × 10 ⁻⁵	
Dubinin-Astakhov (DA) equation							
System	q ^o (kg /kg)		E (J/mol)			n	
AQSOA-Z01 + Water	0.21		4000			5	
AQSOA-Z02 + Water	0.285		7600			2.9	
AQSOA-Z05 + Water	0.22		2700			6	
Modified Langmuir isotherm equation							
System	q ^o (kg/kg)	z	β	α	t ₁	n ₁	ϕ _m (J/mol)
AQSOA-Z01 + Water	0.21	3	0.6	0.002479	2	-1.5	520
AQSOA-Z02 + Water	0.29	2.6	0.5	0.005517	2	0.5	250
AQSOA-Z05 + Water	0.22	3	1	0.011109	1.5	-3.5	250

5.2.3 Summary

This Chapter describes experimentally measured adsorption isotherms data employing both the volumetric and gravimetric method and these data are fitted with various isotherm equations. Based on isotherm data and the thermodynamic frameworks of adsorbate – adsorbent potentials, the next chapter develops a thermodynamic formulation from which the performance parameters of adsorption cooling and desalination system are calculated as a function of pore width and pore volume of adsorbent structure.

Employing isotherm data and isosteric heat as a function of pore width, the energetic performances of adsorption assisted cooling and desalination in terms of COP and SWP are calculated. The next chapter shows the thermodynamic frameworks of adsorption cooling and desalination, where the COP and SWP are shown in terms of pore width for activated carbons – CO₂, silica gel – water systems.

Chapter 6 Thermodynamic Frameworks for Adsorption Cooling and Desalination Systems

This chapter presents the thermodynamic frameworks for the calculation of coefficient of performance (COP), overall performance ratio (OPR) and the specific water production (SWP) as a function of pore width and volume of the adsorbent material. The performance parameters are calculated employing the formulations of isosteric heat at zero coverage and adsorbate uptake. Based on CO₂ and water uptakes with the interaction potentials between various adsorbent – adsorbate systems such as activated carbons – CO₂, silica gel – water, the energetic performances are presented.

6.1 Thermodynamic Framework of Adsorption Cooling and Desalination

The adsorption chiller uses adsorbent – adsorbate characteristics and produces cooling effect at the evaporator by the amalgamation of adsorption-triggered-evaporation and desorption-activated-condensation. This means that for continuous cooling purposes, the evaporated refrigerants are adsorbed into the adsorbent pores and results in the heat of adsorption. During desorption phase, the refrigerant, i.e., water vapour is desorbed (due to heat applied in the adsorber heat exchanger), and the desorbed water vapour is condensed in the condenser, and finally, the condenser water is refluxed back to the evaporator for the next cycle. On the other hand, the condensed water can be collected for desalination cycle, e.g., continuous production of desalinated water. It should be noted here that the adsorber (heat exchanger) is comprised of a copper tube – fin assembly where the porous adsorbents are housed with binders and stainless steel mesh.

The schematic diagram of the two-bed adsorption cooling system with porous adsorbents (activated carbon for example) and adsorption bed or heat exchanger are shown in Figure 6.1 [10].

Figure 6.1 The schematic of adsorption chiller for continuous cooling

For explaining the mathematical modelling of adsorption assisted cooling and desalination, a general overview in pressure-temperature-uptake co-ordinate system is shown in Figure 6.2

Figure 6.2 The schematic of adsorption - desorption processes in the adsorption bed employing pressure - temperature - uptakes co-ordinate system. Here the process A indicates the pressurisation in the adsorption bed with the effects of un-adsorbed adsorbate in void volume, B defines the flow out of high pressurised CO₂ from the adsorption cell, the process C occurs due to the decrease of pressure in the adsorption bed and D indicates low pressure adsorbate flow into the sorption cell [10].

The amount of water uptake in terms of characteristics of adsorbent (e.g., pore width and volume) is given by [45],

$$q = v_p \rho_l \exp \left[- \left\{ \frac{\ln(P_s/P)}{1 - (N_A \bar{V}_{\text{ext}}/RT) - (q_{st}/RT)} \right\}^n \right] \quad (6.1)$$

where v_p is pore volume, ρ_l is liquid water density, P_s is the saturation pressure at temperature and the Boltzmann average external wall potential is given by,

$$\bar{V}_{\text{ext}} = \int_0^H V_{\text{ext}}(z) \exp \left\{ - \frac{V_{\text{ext}}(z)}{kT} \right\} dz / \int_0^H \exp \left\{ - \frac{V_{\text{ext}}(z)}{kT} \right\} dz \quad (6.2)$$

By applying the adsorption, desorption, evaporation and condensation conditions to the equation, the water uptakes and offtakes during adsorption and desorption are calculated as,

$$q_{ads} = v_p \rho_l \exp \left[- \left\{ \frac{\ln(P_s(T_{ads})/P_{evap})}{1 - (N_A \bar{V}_{ext}/RT_{ads}) - (q_{st}/RT_{ads})} \right\}^n \right] \quad (6.3)$$

$$q_{des} = v_p \rho_l \exp \left[- \left\{ \frac{\ln(P_s(T_{des})/P_{cond})}{1 - (N_A \bar{V}_{ext}/RT_{des}) - (q_{st}/RT_{des})} \right\}^n \right] \quad (6.4)$$

For continuous cooling operation, firstly a low-pressure refrigerant is evaporated at the evaporator due to external cooling load (or chilled water or cooling coil). The cooling capacity in kW (Q_{evap}) is calculated as,

$$Q_{evap} = \int_{q_{des}}^{q_{ads}} h_{fg}(T_{evap}) dq - \int_{q_{des}}^{q_{ads}} \int_{T_{evap}}^{T_{cond}} (c_{p,l} dT) dq - \int_{q_{des}}^{q_{ads}} \{h_g(P, T) - h_g(T)\} dq \quad (6.5)$$

The first term of the right-hand-side of the equation indicates the enthalpy of vaporization, the second term defines the amount of condensed heat that enters in to the evaporator, and the third term occurs due to the non-ideality of gaseous phase. Here the subscripts “ads” indicates the adsorption, “des” denotes desorption, “evap” is the evaporation and “cond” stands for the condensation. After evaporation, the refrigerant is adsorbed on the pores of solid adsorbent at relatively low pressure. Within the adsorption bed the heat of adsorption is released, which results in heating up the adsorbent and the adsorber heat exchanger. This heat of adsorption is removed by the cooling fluid during the adsorption phase. Secondly, the adsorbed vapour is released by supplying heating fluid to the pipes of sorption heat exchanger. As a result, the pressure and temperature of the adsorption bed increase up to P_{cond} and T_{des} (process AB of Figure 6.2), and the desorbed refrigerant enters into the condenser for condensation. During the desorption stage, the amount of heat (Q_{des}) added to the sorption bed is calculated by [149],

$$\begin{aligned}
Q_{des} = & \int_{T_{ads}}^{T_{reg}} \left[c_{p,s} + q_{ads} \left\{ c_{p,l} + q_{st} \left(\frac{1}{T} - \frac{1}{v_g} \frac{dv_g}{dT} \right) \right\} \right] dT + \int_{q_{des}}^{q_{ads}} \{ h_a(P, T, q) - h_g(T) \} dq \\
& + \int_{P_{evap}}^{P_{cond}} q_{st} \frac{\partial q}{\partial P} |_T dP \\
& + \int_{T_{reg}}^{T_{des}} \left[c_{p,s} + q_{des} \left\{ c_{p,l} + q_{st} \left(\frac{1}{T} - \frac{1}{v_g} \frac{dv_g}{dT} \right) + q_{st} \frac{\partial q}{\partial T} |_P \right\} \right] dT \quad (6.6)
\end{aligned}$$

where c_p is the specific heat, v is the specific volume and h is the enthalpy. T_{reg} indicates the regeneration temperature at the beginning of desorption periods. The subscripts “a”, “s”, “g” and “l” indicate adsorbate, solid, gaseous and liquid phases. The first term of the right hand side of Equation (6.6) indicates the sensible heat input per unit mass of adsorbent (M_s) due to specific heat of adsorbent and its associate adsorbate for the temperatures ranging from T_{ads} to T_{reg} . The second terms indicate (i) the change in enthalpy with respect to the adsorbed and gaseous phases, and (ii) the isosteric heat due to change in pressures from P_{evap} to P_{cond} . The last terms define sensible heats for the temperatures varying from T_{reg} to T_{des} .

The heat of condensation is given by,

$$Q_{cond} = \int_{q_{des}}^{q_{ads}} h_{fg}(T_{cond}) dq - \int_{q_{des}}^{q_{ads}} \int_{T_{evap}}^{T_{cond}} (c_{p,l} dT) dq + \int_{q_{des}}^{q_{ads}} \{ h_g(P, T) - h_g(T) \} dq \quad (6.7)$$

The first term of the right hand side of the equation indicates the heat released by the condensed water, the second term is the amount of heat brought to evaporator from condenser and the last term occurs due to the non-ideality of gaseous phase.

Employing the thermodynamic property fields of an adsorbent-adsorbate system [149], the enthalpy of adsorbed phase is given by

$$h_a \approx h(P, T, q = 0) + \int_{T_0}^T \left[q_{st} \left(\frac{1}{T} - \frac{1}{v_g} \frac{dv_g}{dT} \right) - \frac{\partial q_{st}}{\partial T} \right] dT + \int_0^q (h_g - q_{st}) dq \quad (6.8)$$

It should be noted here that $\Delta q (= q_{ads} - q_{des})$ is the amount of CO₂ refrigerant that can be delivered from the adsorption cell per adsorption-desorption cycle.

The performance parameter of adsorption cooling cycle is defined by the coefficient of performance (COP), i.e., (Q_{evap}/Q_{des}) [10], where Q_{evap} and Q_{des} are cooling capacity and the amount of heat added to the sorption bed during desorption stage. The overall performance ratio (OPR) of the adsorption cycle, defined as the ratio of net useful effects (adsorption cooling or desalination) to the useful heat input, given by $(Q_{evap} + Q_{cond})/Q_{des}$ [45].

For desalination, the same adsorption chiller is applied in the simulation and the only difference is that the condensed water will be collected from the condenser instead of flowing back to the evaporator in adsorption cooling cycles. The specific water production (SWP) is calculated as $(q_{ads} - q_{des})$.

6.2 *P-h* (Pressure-Enthalpy) Diagram of Adsorption Assisted Cooling and Desalination

Employing Equation (6.3), the thermodynamic property surfaces of silica gel water system is plotted in a Pressure-enthalpy-uptake (*P-h-q*) co-ordinate system as represented in **Figure 6.3**.

Figure 6.3 P-h diagram of ACCD cycle. Here “o” indicates our experimental data of type RD silica gel-water system.

From Figure 6.3, one can easily calculate the energetic performances of the adsorption cycle in terms of cooling capacity and water production. Due to the cooling load (Q_{evap}), the enthalpy of evaporation $h_{fg}(=h_H - h_G)$ at the evaporator and the evaporated water vapor is adsorbed in silica gel surfaces of sorption bed (H-A). During the regeneration phase (lines A-B-C), the pressure in the adsorber rises from evaporator pressure (P_{evap}) to condenser pressure (P_{cond}) and the desorption of water vapour from silica gels occurs by connecting the adsorption bed with the condenser. The amount of uptake falls from q_{ads} to q_{des} , and the enthalpy of adsorbed phase changes from h_A to h_C . At the condenser, the water vapour is condensed and heat is released to the environment. The amount of condensed water is calculated by $M_{sg}(q_{ads}-q_{des})$, where M_{sg} is the mass of silica gel. During that phase, the enthalpy changes from h_C to h_F . Finally the condensed water goes to the fresh water tank and completes the cycle. During the adsorption phase (lines C-

D-A), the sorption bed is cooled and the pressure falls from P_{cond} to P_{evap} . The refrigerant vapour is adsorbed on the adsorbent and the amount of water is increased to q_{ads} .

6.3 Performances of Silica Gel – Water based Cooling and Desalination

For the silica gel water system, the Toth isotherm equation is employed to calculate the amount of water vapour uptakes and offtakes under adsorption chiller operating conditions. The maximum water uptakes are related to the adsorbent pore volume. The experimental data and the fitted isotherms modellings are provided in Chapter 5. The isosteric heats as a function of pore widths are also described in Chapter 4 in detail. In Chapter 3, it is observed that a rapid change in isosteric heat at zero coverage (q_{st}^0) occurs for pore sizes smaller than 3 Å. For larger pores, there is a rapid decrease in q_{st}^0 .

Figure 6.4 shows the COP as a function of pore width for various micropore volumes of silica gels. According to Figure 6.4, the COP is an increasing function of pore width up to the micro and mesopore ranges, and an increase of the total micropore volume (v_p) leads to the improvement of the COP. This improvement is due to an increase of the mass of refrigerant exchanged during the adsorption cooling cycle, which indicates that the structural characteristics of silica gel affect the performances of adsorption cooling cycle.

Figure 6.4 COP as a function of total micropore volume ranged from 0.3 to 0.6 cc/g and pore size for the regeneration temperature of 353 K. Here cc indicates cm^3 .

Figure 6.5 shows the COP as a function of pore volume for various regeneration temperatures. An increase of the total micropore volume leads to an improvement of the COP due to an increase of the mass of water vapour exchanged during the cycle. The experimentally measured COP data as a function of regeneration temperatures are also plotted for comparisons. The influences of the pore width against the specific water production (SWP, kg of water per kg of silica gel) for various pore volumes and the evaporator temperature of 280 K are shown in Figure 6.6 It is found that the maximum amount of water is obtained for the pore widths ranging from 0.8 nm to 1 nm. This is valid for all types of silica gels at the evaporator temperature varying from 278 K to ambient temperature.

Figure 6.5 A plot of COP versus desorption temperature for various types of silica gels.

Figure 6.6 Influences of pore widths on water production for the evaporator temperature of 280 K. Pore volume is ranged from 0.2 to 0.7 cc/g and here cc indicates cm^3 .

From literature, it is found that both ‘RD’ and ‘A’ types silica gels have similar pore size distribution curves and their local maxima are experimentally observed at 1.1 nm and 1.2 nm, respectively. This means that the pore widths ranging from 0.8 to 1.2 provide the best performance in terms of COP and SWP (Figure 6.4 and Figure 6.6). It should also be noted here that in the meso-pore ranges (pore width > 2 nm), the adsorption and desorption rates of water vapour on the silica gel adsorbent becomes slow and it takes longer cycles and switching times to complete the adsorption cycle, and the performances of the cooling and desalination drops.

The specific water production (SWP) for various heat source temperatures is shown in Figure 6.7.

Figure 6.7 A plot of SWP against pore width for various evaporator temperatures. Here the evaporator temperatures range from 274K to 303 K and the regeneration temperature is 353 K. For evaporator temperatures ranging from 274 K to 288 K, the maximum SWP is obtained for the pore width of 0.9 nm. These variations occur due to the isosters moving as a function of isosteric heats. The SWP increases with higher evaporator temperature.

The overall performance ratio (OPR) of the adsorption cycle, defined as the ratio of net useful effects to the useful heat input, is shown in Figure 6.8. As there are two useful effects namely the cooling and the desalinated water, a high OPR is expected. It could have a value of 1.1 at the evaporator temperature of 280 K (as a suitable temperature for cooling and desalination) for the pore width and volume of 0.9 nm and 0.45 cm³/gm. This is valid for type RD silica gel.

Figure 6.8 Overall performance ratio as a function of pore width for various pore volumes of silica gel. Pore volume is ranged from 0.2 to 0.7 cc/g.

6.4 Performances of Activated Carbons – CO₂ based Cooling and Refrigeration

In an adsorption cooling cycle, the relative pressure (P/P_s) ranges from 0.1 to 0.2 which is a small portion of the full pressure range i.e. P_{evap} and P_{cond} are very small as compared with their saturation values. So the concept of isosteric heat at zero coverage as a function of pore widths can be applied to calculate the performances of adsorption chiller. Employing the relationship

between the Henry's coefficient and the external adsorbent potential as a function of pore width direction (y), the isosteric heat of adsorption at Henry's region is given by

$$q_{st}^o = RT - N_A \frac{\int_0^H V_{\text{ext}}(z) e^{\left(-\frac{V_{\text{ext}}(z)}{kT}\right)} dz}{\int_0^H e^{\left(-\frac{V_{\text{ext}}(z)}{kT}\right)} dz} \quad (6.9)$$

where V_{ext} defines the average external potential of adsorbent + adsorbate (please refer to **Chapter 3** for more detailed analysis). The V_{ext} occurs due to the effects of adsorbent – adsorbate and adsorbate – adsorbate interactions with the presence of coulomb forces. k_b is the Boltzmann constant and H_c is the pore width of solid adsorbents. The mathematical expression of V_{ext} for adsorbent – adsorbate interactions is given by

$$V_{\text{ext}}(y) = \phi_{sf}(y) + \phi_{sf}(H - y) \quad (6.10)$$

Here $H(=H_c - \sigma_{ss})$ is the pore width, H_c is the distance between centres of carbon on opposing wall and σ_{ss} is the size of carbon atom. The interactive potential between an adsorbate molecule and carbon wall (ϕ_{sf}) is written as [105]

$$\phi_{sf} = 2\pi\epsilon_{sf}\rho_s\sigma_{sf}^2\Delta\left[\frac{2}{5}\left(\frac{\sigma_{sf}}{y}\right)^{10} - \left(\frac{\sigma_{sf}}{y}\right)^4 - \left(\frac{\sigma_{sf}^4}{3\Delta(0.61\Delta + y)^3}\right)\right] \quad (6.11)$$

where y is the distance of the adsorbate molecule to carbon wall surface, ϵ_{sf} is the fluid-solid well depth, ρ_s is the carbon density, σ_{sf} is the fluid-solid collision diameter, Δ is the separation between carbon layer. The fluid-solid well depth ϵ_{sf} and collision diameter σ_{sf} are obtained using the Lorentz–Berthelot combining rules, i.e., $\epsilon_{sf} = \sqrt{\epsilon_{ss}\epsilon_{ff}}$ and $\sigma_{sf} = \frac{\sigma_{ss} + \sigma_{ff}}{2}$, where ϵ_{ss} is the well depth of carbon, ϵ_{ff} is the well depth of adsorbate molecule (here CO_2), σ_{ss} is the

size of carbon atom and σ_{ff} is the size of CO₂ molecule. The parameters used to calculate the isosteric heat of adsorption are furnished in Table 6.1

Table 6.1 Parameters of activated carbon and CO₂ adsorbate molecules for simulation purposes

Activated Carbon				
Δ (Å)	ρ_s (Å ⁻³)	ε_{ss}/k_b (K)	σ_{ss} (Å)	References
3.35	0.114	28	3.4	[150]
Carbon Dioxide				
Molecules	Group	ε_{ff}/k_b (K)	σ_{ff} (Å)	References
CO ₂	C	28.129	3.49	[151]
	O	80.507	3.13	[151]

Figure 6.9 The plot of isosteric heat of adsorption as a function of pore width for the adsorption of CO₂ on carbonaceous material

Here we consider mainly the effects of solid – fluid interactions to calculate the q_{st}^o . The plot of q_{st}^o versus pore width is shown in Figure 6.9. It is observed that a rapid change in q_{st}^o occurs for pore sizes that are smaller than the pore size at which the maximum q_{st}^o is occurred due to the overlap of the force fields from opposite walls of the micropores. The value of q_{st}^o decreases

when the size of the pore increases i.e. in other words, for larger pores, there is a rapid decrease in q_{st}^0 . In this section, the experimental isotherm data of activated carbon (type ACF-A20, Maxsorb III, BPL AC and monolithic carbon) and Toth isotherm parameters with CO₂ as presented in Chapter 5 are used to highlight the present findings.

It should be noted here that the amount of CO₂ uptakes and offtakes depend on the evaporator pressure and the condenser pressure with respect to the designed heat source and heat sink temperatures. The adsorption cooling cycle ranges from P_{evap} to P_{cond} . The net amount of CO₂ refrigerant per adsorption cooling cycle varies from q_{ads} and q_{des} . Here q_{ads} is measured as a function of P_{evap} and T_{ads} , where $T_{ads} = 31$ °C and P_{evap} is the saturation pressure of cooling load temperature that varies from -5 °C to 15 °C. On the other hand, q_{des} is calculated with respect to P_{cond} and T_{des} , where P_{cond} is the saturated pressure at 31 °C and T_{des} ranges from 60 to 110 °C.

The cooling effect is not achieved if the heating source temperature is considered as room temperature. For example, the minimum desorption temperature is 55 °C for the cooling load and heat sink temperatures of 10 °C and 31 °C, respectively. The system performances (COP) against pore widths of various activated carbons are plotted in Figure 6.10. Hence the COP is presented for the heating source temperatures ranging from 60 °C to 110 °C. As can be seen from Figure 6.10(a) – (d), the COP is an increasing function of pore width up to (a) 10 Å for Maxsorb III AC, (b) 11 Å for activated carbon fiber (A-20), (c) 8 Å for BPL activated carbon, and (d) 15 Å for the monolithic activated carbon. The COP decreases slightly at larger pore widths due to the adsorptive sites of decreasing energy. In the micropores, the amount of CO₂ uptake increases due to higher force field in the adsorbent structure or in other words the mass of CO₂ refrigerant per adsorption cooling cycle is also increased. Therefore the higher cooling capacity as well as the

maximum COP is found in the micropore ranges. At super-micropore ranges (3 Å to 5 Å), the COP drops significantly due to weak interactions between carbon and CO₂ molecules.

Figure 6.10 COP against pore widths for (a) pitch based activated carbon (Maxsorb III), (b) activated carbon fibre (ACF-A20), (c) BPL activated carbon and (d) monolith activated carbon based adsorption cooling cycle for the heat source temperatures ranging from 60°C to 110°C at the cooling load and the heat sink temperatures of 10°C and 30°C, respectively.

Figure 6.11 The COP of ADC as a function of pore widths at various cooling load temperatures for the adsorption of CO₂ on (a) Maxsorb III, (b) ACF (A-20), (c) BPL activated carbon and (d) monolith activated carbon. Here the driving heat source and the heat sink temperatures are 90 °C and 10 °C, respectively.

Figure 6.11(a) – (d) show the COP against pore widths for the adsorption of CO₂ on (a) Maxsorb III activated carbon (b) ACF (type A-20), (c) BPL AC and (d) monolithic AC for various cooling load temperatures at the heat source and the heat sink temperatures of 90°C and 10°C, respectively. The COP increases at higher evaporator temperatures due to the transfer of more refrigerant per adsorption cooling period. No cooling effects are achieved for pore widths below 3 Å as the CO₂ molecules cannot penetrate into the pores of adsorbents during adsorption. The

COP decreases gradually for larger pore widths. The adsorbate molecules are gradually accommodated in larger pores, in which the adsorption affinity becomes weaker. Therefore, a monotonic decrease in COP against pore widths is observed. The predictions for the maximum COP of adsorption cooling cycle employing carbonaceous materials and CO₂ are shown in Table 6.2

Table 6.2 The optimum COP of activated carbons + CO₂ assisted adsorption cooling cycle for various heat source temperatures at the cooling load and the heat sink temperatures of 10 °C and 30 °C

Adsorbent – adsorbate system	Pore width (Å)	Average COP at various heat source temperatures					
		60 °C	70 °C	80 °C	90 °C	100 °C	110 °C
Maxsorb III – CO ₂	7 ~ 15 Å	0.28	0.40	0.51	0.60	0.67	0.73
ACF (A-20) – CO ₂	8 ~ 12 Å	0.19	0.30	0.40	0.46	0.51	0.55
BPL AC – CO ₂	7 ~ 10 Å	0.33	0.45	0.53	0.58	0.62	0.65
Monolith AC – CO ₂	10 ~ 20 Å	0.06	0.13	0.18	0.21	0.24	0.26

It is found that the COP is an increasing function of heating source temperatures. The pore width generally ranges from 7 to 15 Å for maximum COP. Most carbonaceous adsorbents such as Maxsorb III, ACF, BPL AC and monolith AC consist of micro, meso and macropores. Both Maxsorb III and ACF possess more micro adsorptive sites where the overlapping interactions of CO₂ molecules increase during adsorption. On the other hand, the BPL activated carbon contains comparatively less adsorption sites with small pore volume. Therefore a sharp decrease in COP occurs in the meso and macro pores. The pore size of monolith AC ranges from 5 Å to 200 Å [152] and it shows relatively lower COP due to smaller pore volume with larger pore sizes. For monolith AC, the optimum COP is found at 15 Å. There are low or no cooling effects at the macro-pore zones or the pore width below 3 Å.

6.5 Summary

From the present analysis, it is noticed that silica gels optimised with respect to pore sizes and volumes for a given evaporating temperature can entail an increase of the COP and OPR of the order of 20 to 40%, which cannot be neglected. If the evaporator temperature varies and especially when it decreases, there is a decreasing tendency of COP. Another conclusion of this study is that an increase of pore volume does not entail systematically an improvement of performance. The best performance of adsorption cooling cycle is obtained from a compromise between the greatest pore volume and the optimal pore size. From the present analysis, it is observed that there is no cooling and water production performance for pore widths varying from 0 to 0.3 nm. For better efficiency, the silica gel should be designed with the pore size of 2 nm.

For cooling and refrigeration purposes, the carbonaceous materials should be designed with micro-pores ranging from 7 to 15 Å and higher micro-pore volume. The knowledge of isosteric heat at zero coverage for an adsorbent – adsorbate system can help in the design of new carbonaceous materials such as carbon nanotubes, carbon fibres, pitch based activated carbon, metal organic frameworks, and carbon–silica composites. From the present analysis, we can approximately find the optimum ranges of pore widths that would be desirable to design porous activated carbons for the adsorption of carbon dioxide on carbon materials in refrigeration and cooling applications. The overall conclusions and future directions are presented in the following chapter.

Chapter 7 Conclusions and Future Work

7.1 Conclusions

In this thesis, a thermodynamic framework for calculating the isosteric heat of adsorption at Henry's region has been derived and developed for various adsorbent + adsorbate systems. The construction of adsorbent molecular structure and adsorbates with various orientations were achieved at first. Secondly, the pore models based on the molecular structures of adsorbent have been proposed. Thirdly, the total interaction potential between adsorbent and adsorbate are computed. Finally, the isosteric heat of adsorption at zero coverage in terms of adsorbent – adsorbate interactions and pore width, is calculated and compared with experimentally measured data.

Employing the proposed thermodynamic frameworks, the connections between the isosteric heat and the parameters such as pore width of adsorbent structure have been established. Finally, the thermodynamic performances such as COP and OPR are evaluated for adsorption assisted cooling and desalination systems.

The thermodynamic framework is built and applied to adsorbent materials of various structures. Firstly, the graphite structure is considered as simple layers of lattice with parallel slit-shaped pore model [14]. The total interaction potential between graphite and polar molecules (such as water, methanol and ethanol) and nonpolar molecules [10] (such as CO₂) are obtained employing the reduced energy expansion equation [107, 153] for polar molecules with various orientations. The isosteric heat of adsorption is derived with respect to the pressure-uptake-temperature co-ordinate system [13]. It is found that the maximum potential well for graphite – water system constitutes 91.28% Lennard Jones potential $v_{LJ}(C\cdots H_2O)$, 8.7% induction potential $v_I(C\cdots H_2O)$ and 0.012% electrostatic $v_E(C\cdots H_2O)$. The maximum potential well depth depends on various

orientations of H₂O molecule on graphite structure. The maximum q_{st}^o at zero surface coverage is found to be 0.35 eV at orientation 1, where the oxygen atom is at the origin, one H atom is at the X-axis and H – O – H is obtained in the X-Y plane, and the simulation result is very close to the experimental data of 0.32 eV. For water molecules, the electrostatic contribution for $v(z)$ is very close to zero and provides attractive or repulsive interactions between adsorbate and graphite molecules. For ethanol and methanol, the electrostatic contribution is close to zero and provides both attractive and repulsive interactions. The $vLJ(C\cdots CH_3-OH)$ and $vLJ(C\cdots CH_3-CH_2-OH)$ contributions are more than 90%. The induction interactions are less than 10%. For both methanol and ethanol molecules, the induction potential increases exponentially for the separation distance decreasing from 3 Å to 0. However, the electrostatic potential remains constant and the value is very close to zero.

Secondly, the amorphous silica structure is constructed [110] by the Reverse Monte Carlo (RMC) [99] simulation tool with experimentally measured X-ray Diffraction (XRD) data of silica sample [109]. The crystallographic properties including partial and total radial distribution and bond angles of the constructed silica structure are compared to experimental results. For simplicity, the simple slit-shaped pore model and Clausius - Clapeyron equation are applied to calculate the isosteric heat of adsorption of water on silica surface. It is found that the partial radial distribution and structure factor of the reference silica structure constructed by Reverse Monte Carlo method are calculated to confirm the validity of SiO₂ structure for q_{st}^o calculation. Furthermore, the bond angle (O-Si-O and Si-O-Si) distribution functions of the silica structure are calculated. The O-Si-O and Si-O-Si angles are mainly around 104° ~112° and 130° ~145° and are in good agreement with other simulation results while the most probable bond angle (MPBA) of Si-O-Si is found to be 146° and that of O-Si-O is 109.4° [112]. The interaction

potential is also determined by the water-silica distance z according to the interaction potential of five positions in orientation 1, which are chosen in the simulation box due to the fact that the centre $x = -11.5 \text{ \AA}$ and $y = -11.5 \text{ \AA}$ is a favorable adsorptive site due to the presence of the negative interaction potential. While the x coordinate is varied from $-11 \text{ \AA}$ to $-12 \text{ \AA}$ and y coordinate is remained fixed at $-11.5 \text{ \AA}$, the maximum interaction potential ranges from -0.782 eV to -0.677 eV .

Thirdly, the molecular structures of three types of zeolites (AQSOA-Z01, Z02 and Z05 [115-117]) are generally considered as cylindrical channel frameworks. The interaction potential between water molecule and the surfaces of these channels are calculated employing the cylindrical interaction potential equation [118-120] with two zeotype parameters (AFI type for Z01 and Z05, CHA type for Z02). The isosteric heat of adsorption of water on AQSOA-Z01, Z02 and Z05 zeolites are calculated employing the modified Clausius – Clapeyron for cylindrical pore model. The most favourable adsorptive sites with negatively larger potentials are identified at the positions of channels inside the zeolite framework. The isosteric heat of adsorption for water adsorption on CHA and AFI types zeolites are predicted to be (a) 50 kJ/mol and 80 kJ/mol respectively employing Steele's interaction potential equation, and (b) 36.26 kJ/mol and 51.4 kJ/mol respectively employing cylindrical interaction potential equation.

All of the theoretically derived isosteric heats are compared with experimental data in the literature. Particularly, the isosteric heats are derived from our experimentally measured adsorption isotherms of calorimetric analysis.

In this thesis, the porous properties of various activated carbons are measured in terms of pore size, pore volume and material structures to understand the nature of these activated carbon materials. A volumetric method is employed to measure the amount of CO_2 uptakes on various

activated carbons. The Tóth isotherm model is fitted with the experimental data within the acceptable error ranges. The formulations of interactive potential between CO₂ molecules and the carbon wall are used to calculate the isosteric heat of adsorption as a function of pore widths. Employing adsorption isotherms and Qst models, a thermodynamic framework is developed to calculate the energetic performance or COP of adsorption cycle. The COP is presented here as a function of pore width. It is observed that there is no cooling performance for pore widths varying from 0 to 3 Å. The best performance is obtained for the pore widths ranging from 7 to 15 Å with higher limiting uptakes or pore volumes. This is found to be higher in micro-pore ranges. This indicates that the adsorption and desorption rates are faster in micro-pores. The carbonaceous materials should be designed with micro-pores ranging from 7 to 15 Å and higher micro-pore volume for adsorption cooling applications. The knowledge of q_{st}^o for an adsorbent – adsorbate system can help in the design of new carbonaceous materials such as carbon nanotubes, carbon fibres, pitch based activated carbon, metal organic frameworks, and carbon–silica composites. From the present analysis, we can approximately find the optimum ranges of pore widths that would be desirable to design porous activated carbons for the adsorption of carbon dioxide on carbon materials in refrigeration and cooling applications.

From the present analysis, it is noticed that silica gels optimised with respect to pore sizes and volumes for a given evaporating temperature can entail an increase of the COP and OPR of the order of 20 to 40%, which cannot be neglected. If the evaporator temperature varies and especially when it decreases, there is a decreasing tendency of COP. Another conclusion of this study is that an increase of pore volume does not entail systematically an improvement of performance. The best performance of adsorption cooling cycle is obtained from a compromise between the greatest pore volume and the optimal pore size. From the present analysis, it is

observed that there is no cooling and water production performance for pore widths varying from 0 to 0.3 nm. The best performance of silica gel-water based cooling and desalination is obtained at the pore width of 0.9 nm with higher pore volume. The isosteric heat is found to be higher in micro-pore ranges. This indicates that the adsorption and desorption rates are higher in micro-pores. The adsorbent materials like silica gel should be designed with micro-pores ranging from 0.8 to 1 nm and higher micro-pore volume for adsorption cooling and desalination applications.

7.2 Future Work

In the future, the following works can be carried out for the further improvement of modelling, simulation and performance optimisation of adsorption assisted cooling and desalination system.

1. To develop advanced molecular structure models for other types of adsorbent materials such as metal organic or other zeolite assisted frameworks that are more complicated than the lattice, amorphous surfaces and framework with channels.
2. To derive a pore model employing the real structure of porous material other than the simplified parallel slit-shaped and cylindrical pore models.
3. To investigate the phase transition and phase equilibrium for polar gas and solid surfaces with complicated molecular structures [154-159].
4. To design and fabricate novel adsorbent materials employing the proposed model and use them for the fabrication of adsorption chillers.

References

- [1] Dąbrowski, A., *Adsorption — from theory to practice*. Advances in Colloid and Interface Science, 2001. **93**(1–3): p. 135-224.
- [2] Wang, X.L.;Cai, W.J.;Lu, J.G.;Sun, Y.X.;Ding, X.D., *A hybrid dehumidifier model for real-time performance monitoring, control and optimization in liquid desiccant dehumidification system*. Applied Energy, 2013. **111**: p. 449-455.
- [3] Ng, K.C.;Thu, K.;Kim, Y.;Chakraborty, A.;Amy, G., *Adsorption desalination: An emerging low-cost thermal desalination method*. Desalination, 2013. **308**: p. 161-179.
- [4] Ng, K.C.;Thu, K.;Saha, B.B.;Chakraborty, A., *Study on a waste heat-driven adsorption cooling cum desalination cycle*. International Journal of Refrigeration-Revue Internationale Du Froid, 2012. **35**(3): p. 685-693.
- [5] Do, D.D., *Adsorption Analysis : Equilibria and Kinetics*. Series on chemical engineering. 1998, London: Imperial College Press. xxi, 892 p.
- [6] Chakraborty, A.;Leong, K.C.;Thu, K.;Saha, B.B.;Ng, K.C., *Theoretical insight of adsorption cooling*. Applied Physics Letters, 2011. **98**(22).
- [7] Brunauer, S.;Deming, L.S.;Deming, W.E.;Teller, E., *On a theory of the van der Waals adsorption of gases*. Journal of the American Chemical Society, 1940. **62**: p. 1723-1732.
- [8] Donohue, M.D.;Aranovich, G.L., *Classification of Gibbs adsorption isotherms*. Advances in Colloid and Interface Science, 1998. **76–77**: p. 137-152.
- [9] Chakraborty, A.;Saha, B.B.;Koyama, S.;Ng, K.C., *On the thermodynamic modeling of the isosteric heat of adsorption and comparison with experiments*. Applied Physics Letters, 2006. **89**(17).

- [10] Fan, W.;Chakraborty, A.;Kayal, S., *Adsorption cooling cycles: Insights into carbon dioxide adsorption on activated carbons*. Energy, 2016. **102**: p. 491-501.
- [11] Saha, B.B.;Chakraborty, A.;Koyama, S.;Aristov, Y.I., *A new generation cooling device employing CaCl₂-in-silica gel-water system*. International Journal of Heat and Mass Transfer, 2009. **52**(1-2): p. 516-524.
- [12] Tian, Y.;Wu, J., *Differential Heat of Adsorption and Isotheres*. Langmuir, 2017. **33**(4): p. 996-1003.
- [13] Schindler, B.J.;Levan, M.D., *The theoretical maximum isosteric heat of adsorption in the Henry's law region for slit-shaped carbon nanopores*. Carbon, 2008. **46**(4): p. 644-648.
- [14] Fan, W.;Chakraborty, A., *Investigation of the Interaction of Polar Molecules on Graphite Surface: Prediction of Isosteric Heat of Adsorption at Zero Surface Coverage*. The Journal of Physical Chemistry C, 2016. **120**(41): p. 23490-23499.
- [15] Foo, K.Y.;Hameed, B.H., *Insights into the modeling of adsorption isotherm systems*. Chemical Engineering Journal, 2010. **156**(1): p. 2-10.
- [16] Ho, Y.S.;McKay, G., *Kinetic Models for the Sorption of Dye from Aqueous Solution by Wood*. Process Safety and Environmental Protection, 1998. **76**(2): p. 183-191.
- [17] Thu, K.;Kim, Y.D.;Myat, A.;Chakraborty, A.;Ng, K.C., *Performance investigation of advanced adsorption desalination cycle with condenser-evaporator heat recovery scheme*. Desalination and Water Treatment, 2013. **51**(1-3): p. 150-163.
- [18] Kayal, S.;Sun, B.C.;Saha, B.B., *Adsorption characteristics of AQSOA zeolites and water for adsorption chillers*. International Journal of Heat and Mass Transfer, 2016. **92**: p. 1120-1127.

- [19] Sah, R.P.;Choudhury, B.;Das, R.K., *A review on adsorption cooling systems with silica gel and carbon as adsorbents*. Renewable and Sustainable Energy Reviews, 2015. **45**: p. 123-134.
- [20] Reddy Panyam, V.;Banker, N.D., *Thermodynamic assessment of a gas turbine power plant integrated with an adsorption refrigeration system*. Applied Thermal Engineering, 2017. **117**: p. 577-583.
- [21] Hamdy, M.;Askalany, A.A.;Harby, K.;Kora, N., *An overview on adsorption cooling systems powered by waste heat from internal combustion engine*. Renewable and Sustainable Energy Reviews, 2015. **51**: p. 1223-1234.
- [22] Ali, S.M.;Chakraborty, A., *Thermodynamic modelling and performance study of an engine waste heat driven adsorption cooling for automotive air-conditioning*. Applied Thermal Engineering, 2015. **90**: p. 54-63.
- [23] Ali, E.S.;Harby, K.;Askalany, A.A.;Diab, M.R.;Alsaman, A.S., *Weather effect on a solar powered hybrid adsorption desalination-cooling system: A case study of Egypt's climate*. Applied Thermal Engineering, 2017. **124**: p. 663-672.
- [24] Alsaman, A.S.;Askalany, A.A.;Harby, K.;Ahmed, M.S., *Performance evaluation of a solar-driven adsorption desalination-cooling system*. Energy, 2017. **128**: p. 196-207.
- [25] Zheng, H., *Absorption and Adsorption Solar Desalination System*. 2017: p. 623-670.
- [26] Alsaman, A.S.;Askalany, A.A.;Harby, K.;Ahmed, M.S., *A state of the art of hybrid adsorption desalination-cooling systems*. Renewable and Sustainable Energy Reviews, 2016. **58**: p. 692-703.
- [27] Brunauer, S.;Emmett, P.H.;Teller, E., *Adsorption of Gases in Multimolecular Layers*. Journal of the American Chemical Society, 1938. **60**(2): p. 309-319.

- [28] Brunauer, S., *The Adsorption of Gases and Vapours*. 1943, London: Geoffrey Cumberlege. vii, 511 p.
- [29] McMillan, W.G.;Teller, E., *The Assumptions of the B.E.T. Theory*. The Journal of Physical Chemistry, 1951. **55**(1): p. 17-20.
- [30] Frenkel, J., *Kinetic theory of liquids*. 1946, Oxford: Clarendon Press. xi, 488 p.
- [31] Halsey, G., *Physical Adsorption on Non - Uniform Surfaces*. The Journal of Chemical Physics, 1948. **16**(10): p. 931-937.
- [32] Hill, T.L., *Theory of Physical Adsorption*, in *Advances in Catalysis*, W.G. Frankenburg, V.I.K.;Rideal, E.K., Editors. 1952, Academic Press. p. 211-258.
- [33] Chakraborty, A.;Sun, B.C., *An adsorption isotherm equation for multi-types adsorption with thermodynamic correctness*. Applied Thermal Engineering, 2014. **72**(2): p. 190-199.
- [34] Sun, B.;Chakraborty, A., *Thermodynamic formalism of water uptakes on solid porous adsorbents for adsorption cooling applications*. Applied Physics Letters, 2014. **104**(20).
- [35] Toth, J., *Adsorption: Theory, Modeling and Analysis*. Surface Science. Vol. 107. 2002, New York: Marcel Dekker Inc.
- [36] Hamdaoui, O.;Naffrechoux, E., *Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon - Part II. Models with more than two parameters*. Journal of Hazardous Materials, 2007. **147**(1-2): p. 401-411.
- [37] Goldberg, S., *Equations and Models Describing Adsorption Processes in Soils*. Chemical Processes in Soils, 2005(chemicalprocess): p. 489-517.
- [38] Lagergren, S., *About the theory of so-called adsorption of soluble substances*. Kungliga Svenska Vetenskapsakademiens. Handlingar, 1898 **24**(4): p. 1-39.

- [39] Ho, Y.S.;McKay, G., *Pseudo-second order model for sorption processes*. Process Biochemistry, 1999. **34**(5): p. 451-465.
- [40] Wu, F.C.;Tseng, R.L.;Juang, R.S., *Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan*. Water Research, 2001. **35**(3): p. 613-618.
- [41] Ho, Y.S.;McKay, G., *Comparative sorption kinetic studies of dye and aromatic compounds onto fly ash*. Journal of Environmental Science and Health, Part A, 1999. **34**(5): p. 1179-1204.
- [42] Lakhlifi, A.;Killingbeck, J.P., *Investigation of the interaction of some astrobiological molecules with the surface of a graphite (0001) substrate. Application to the CO, HCN, H₂O and H₂CO molecules*. Surface Science, 2010. **604**(1): p. 38-46.
- [43] Klomkliang, N.;Kaewmanee, R.;Saimoey, S.;Intarayothya, S.;Do, D.D.;Nicholson, D., *Adsorption of water and methanol on highly graphitized thermal carbon black: The effects of functional group and temperature on the isosteric heat at low loadings*. Carbon, 2016. **99**: p. 361-369.
- [44] Birkett, G.R.;Do, D.D., *Simulation study of methanol and ethanol adsorption on graphitized carbon black*. Molecular Simulation, 2006. **32**(10-11): p. 887-899.
- [45] Chakraborty, A.;Thu, K.;Ng, K.C., *Advanced Adsorption Cooling cum Desalination Cycle: A Thermodynamic Framework*. 2011: p. 605-610.
- [46] Pons, M.;Meunier, F.;Cacciola, G.;Critoph, R.E.;Groll, M.;Puigjaner, L.;Spinner, B.;Ziegler, F., *Thermodynamic based comparison of sorption systems for cooling and heat pumping*. International Journal of Refrigeration, 1999. **22**(1): p. 5-17.
- [47] Chakraborty, A.;Thu, K.;Saha, B.B.;Ng, K.C., *Adsorption-Desalination Cycle*, in *Advances in Water Desalination*. 2012, John Wiley & Sons, Inc. p. 377-451.

- [48] Lu, Z.S.;Wang, R.Z.;Xia, Z.Z.;Gong, L.X., *Experimental investigation adsorption chillers using micro-porous silica gel-water and compound adsorbent-methanol*. Energy Conversion and Management, 2013. **65**: p. 430-437.
- [49] Liu, Y.;Leong, K.C., *Numerical study of a novel cascading adsorption cycle*. International Journal of Refrigeration-Revue Internationale Du Froid, 2006. **29**(2): p. 250-259.
- [50] Thu, K.;Chakraborty, A.;Kim, Y.D.;Myat, A.;Saha, B.B.;Ng, K.C., *Numerical simulation and performance investigation of an advanced adsorption desalination cycle*. Desalination, 2013. **308**: p. 209-218.
- [51] Jribi, S.;Koyama, S.;Saha, B.B., *Performance Investigation of a Novel CO₂ Compression-Adsorption Based Hybrid Cooling Cycle*. . Engineering Sciences Reports, Kyushu University, 2010. **32**(3): p. 12-18.
- [52] Askalany, A.A.;Saha, B.B.;Kariya, K.;Ismail, I.M.;Salem, M.;Ali, A.H.H.;Morsy, M.G., *Hybrid adsorption cooling systems-An overview*. Renewable & Sustainable Energy Reviews, 2012. **16**(8): p. 5787-5801.
- [53] Habib, K.;Saha, B.B.;Chakraborty, A.;Oh, S.T.;Koyama, S., *Study on solar driven combined adsorption refrigeration cycles in tropical climate*. Applied Thermal Engineering, 2013. **50**(2): p. 1582-1589.
- [54] Habib, K.;Saha, B.B.;Chakraborty, A.;Koyama, S.;Srinivasan, K., *Performance evaluation of combined adsorption refrigeration cycles*. International Journal of Refrigeration-Revue Internationale Du Froid, 2011. **34**(1): p. 129-137.
- [55] Lu, Z.S.;Wang, R.Z., *Performance improvement and comparison of mass recovery in CaCl₂/activated carbon adsorption refrigerator and silica gel/LiCl adsorption chiller*

- driven by low grade waste heat. International Journal of Refrigeration-Revue Internationale Du Froid*, 2013. **36**(5): p. 1504-1511.
- [56] Wang, X.L.;Chua, H.T., *Two bed silica gel-water adsorption chillers: An effectual lumped parameter model. International Journal of Refrigeration-Revue Internationale Du Froid*, 2007. **30**(8): p. 1417-1426.
- [57] Chakraborty, A.;Saha, B.B.;Aristov, Y.I., *Dynamic behaviors of adsorption chiller: Effects of the silica gel grain size and layers. Energy*, 2014. **78**: p. 304-312.
- [58] Aristov, Y.I., *Optimal adsorbent for adsorptive heat transformers: Dynamic considerations. International Journal of Refrigeration-Revue Internationale Du Froid*, 2009. **32**(4): p. 675-686.
- [59] Miyazaki, T.;Akisawa, A.;Saha, B.B.;El-Sharkawy, I.I.;Chakraborty, A., *A new cycle time allocation for enhancing the performance of two-bed adsorption chillers. International Journal of Refrigeration-Revue Internationale Du Froid*, 2009. **32**(5): p. 846-853.
- [60] Li, A.;Bin Ismail, A.;Thu, K.;Ng, K.C.;Loh, W.S., *Performance evaluation of a zeolite-water adsorption chiller with entropy analysis of thermodynamic insight. Applied Energy*, 2014. **130**: p. 702-711.
- [61] Qian, S.X.;Gluesenkamp, K.;Hwang, Y.;Radermacher, R.;Chun, H.H., *Cyclic steady state performance of adsorption chiller with low regeneration temperature zeolite. Energy*, 2013. **60**: p. 517-526.
- [62] Restuccia, G.;Freni, A.;Russo, F.;Vasta, S., *Experimental investigation of a solid adsorption chiller based on a heat exchanger coated with hydrophobic zeolite. Applied Thermal Engineering*, 2005. **25**(10): p. 1419-1428.

- [63] Gong, L.X.;Wang, R.Z.;Xia, Z.Z.;Lu, Z.S., *Experimental study on an adsorption chiller employing lithium chloride in silica gel and methanol*. International Journal of Refrigeration-Revue Internationale Du Froid, 2012. **35**(7): p. 1950-1957.
- [64] Saha, B.B.;EI-Sharkawy, I.I.;Chakraborty, A.;Koyama, S., *Study on an activated carbon fiber-ethanol adsorption chiller: Part I - system description and modelling*. International Journal of Refrigeration-Revue Internationale Du Froid, 2007. **30**(1): p. 86-95.
- [65] Jribi, S.;Saha, B.B.;Koyama, S.;Bentaher, H., *Modeling and simulation of an activated carbon-CO₂ four bed based adsorption cooling system*. Energy Conversion and Management, 2014. **78**: p. 985-991.
- [66] Tso, C.Y.;Chao, C.Y.H.;Fu, S.C., *Performance analysis of a waste heat driven activated carbon based composite adsorbent - Water adsorption chiller using simulation model*. International Journal of Heat and Mass Transfer, 2012. **55**(25-26): p. 7596-7610.
- [67] Tso, C.Y.;Chao, C.Y.H., *Activated carbon, silica-gel and calcium chloride composite adsorbents for energy efficient solar adsorption cooling and dehumidification systems*. International Journal of Refrigeration-Revue Internationale Du Froid, 2012. **35**(6): p. 1626-1638.
- [68] Wu, J.W.;Biggs, M.J.;Hu, E.J., *Dynamic model for the optimisation of adsorption-based desalination processes*. Applied Thermal Engineering, 2014. **66**(1-2): p. 464-473.
- [69] Ng, K.C.;Chua, H.T.;Chung, C.Y.;Loke, C.H.;Kashiwagi, T.;Akisawa, A.;Saha, B.B., *Experimental investigation of the silica gel-water adsorption isotherm characteristics*. Applied Thermal Engineering, 2001. **21**(16): p. 1631-1642.
- [70] Mitra, S.;Kumar, P.;Srinivasan, K.;Dutta, P., *Simulation study of a two-stage adsorber system*. Applied Thermal Engineering, 2014. **72**(2): p. 283-288.

- [71] Thu, K.;Saha, B.B.;Chakraborty, A.;Chun, W.G.;Ng, K.C., *Study on an advanced adsorption desalination cycle with evaporator-condenser heat recovery circuit*. International Journal of Heat and Mass Transfer, 2011. **54**(1-3): p. 43-51.
- [72] Thu, K.;Ng, K.C.;Saha, B.B.;Chakraborty, A.;Koyama, S., *Operational strategy of adsorption desalination systems*. International Journal of Heat and Mass Transfer, 2009. **52**(7-8): p. 1811-1816.
- [73] Ng, K.C.;Thu, K.;Oh, S.J.;Ang, L.;Shahzad, M.W.;Bin Ismail, A., *Recent developments in thermally-driven seawater desalination: Energy efficiency improvement by hybridization of the MED and AD cycles*. Desalination, 2015. **356**: p. 255-270.
- [74] Shahzad, M.W.;Ng, K.C.;Thu, K.;Saha, B.B.;Chun, W.G., *Multi effect desalination and adsorption desalination (MEDAD): A hybrid desalination method*. Applied Thermal Engineering, 2014. **72**(2): p. 289-297.
- [75] Thu, K.;Kim, Y.D.;Amy, G.;Chun, W.G.;Ng, K.C., *A hybrid multi-effect distillation and adsorption cycle*. Applied Energy, 2013. **104**: p. 810-821.
- [76] Kim, Y.-D.;Thu, K.;Masry, M.E.;Ng, K.C., *Water quality assessment of solar-assisted adsorption desalination cycle*. Desalination, 2014. **344**: p. 144-151.
- [77] Xu, S.Z.;Wang, L.W.;Wang, R.Z., *Thermodynamic analysis of single-stage and multi-stage adsorption refrigeration cycles with activated carbon-ammonia working pair*. Energy Conversion and Management, 2016. **117**: p. 31-42.
- [78] Wang, L.W.;Metcalf, S.J.;Critoph, R.E.;Thorpe, R.;Tamainot-Telto, Z., *Development of thermal conductive consolidated activated carbon for adsorption refrigeration*. Carbon, 2012. **50**(3): p. 977-986.

- [79] Ghazy, M.;Askalany, A.A.;Harby, K.;Ahmed, M.S., *Adsorption isotherms and kinetics of HFC-404A onto bituminous based granular activated carbon for storage and cooling applications*. Applied Thermal Engineering, 2016. **105**: p. 639-645.
- [80] Werder, T.;Walther, J.H.;Jaffe, R.L.;Halicioglu, T.;Koumoutsakos, P., *On the water-carbon interaction for use in molecular dynamics simulations of graphite and carbon nanotubes*. Journal of Physical Chemistry B, 2003. **107**(6): p. 1345-1352.
- [81] Carlos, W.E.;Cole, M.W., *Interaction between a He atom and a graphite surface*. Surface Science, 1980. **91**(1): p. 339-357.
- [82] Wang, M.X.;Huang, Z.H.;Lv, W.;Yang, Q.H.;Kang, F.Y.;Liang, K.M., *Water vapor adsorption on low-temperature exfoliated graphene nanosheets*. Journal of Physics and Chemistry of Solids, 2012. **73**(12): p. 1440-1443.
- [83] von Alfthan, S.;Kuronen, A.;Kaski, K., *Realistic models of amorphous silica: A comparative study of different potentials*. Physical Review B, 2003. **68**(7): p. 073203.
- [84] Kierys, A.;Goworek, J.;Rawski, M.;Halasz, I., *On the molecular basis of silica gel morphology*. Advanced Materials Letters, 2015. **6**(1): p. 40-46.
- [85] Che, M.;Mori, K.;Yamashita, H., *Elaboration, characterization and properties of silica-based single-site heterogeneous photocatalysts*. Proceedings of the Royal Society a-Mathematical Physical and Engineering Sciences, 2012. **468**(2143): p. 2113-2128.
- [86] Hench, L.L.;West, J.K., *Molecular-Orbital Models of Silica*. Annual Review of Materials Science, 1995. **25**: p. 37-68.
- [87] Bnown, G.E.;Grnns, G.V., *Oxygen Coordination and the Si-O Bond*. American Mineralogist, 1969. **54**: p. 1528-1539.

- [88] Raymonda, J.W.;Muentner, J.S.;Klempere.Wa, *Electric Dipole Moment of Sio and Geo.* Journal of Chemical Physics, 1970. **52**(7): p. 3458-&.
- [89] Liu, J.;Yu, J., *Chapter 1 - Toward Greener and Designed Synthesis of Zeolite Materials A2 - Sels, Bert F*, in *Zeolites and Zeolite-Like Materials*, Kustov, L.M., Editor. 2016, Elsevier: Amsterdam. p. 1-32.
- [90] Ilić, B.;Wettstein, S.G., *A review of adsorbate and temperature-induced zeolite framework flexibility.* Microporous and Mesoporous Materials, 2017. **239**: p. 221-234.
- [91] Liu, Z.;Wakihara, T.;Nomura, N.;Matsuo, T.;Anand, C.;Elangovan, S.P.;Yanaba, Y.;Yoshikawa, T.;Okubo, T., *Ultrafast and Continuous Flow Synthesis of Silicoaluminophosphates.* Chemistry of Materials, 2016. **28**(13): p. 4840-4847.
- [92] Flanigen, E.M.;Lok, B.M.;Patton, R.L.;Wilson, S.T., *Aluminophosphate Molecular-Sieves and the Periodic-Table.* Pure and Applied Chemistry, 1986. **58**(10): p. 1351-1358.
- [93] Bojan, M.J.;Steele, W.A., *Chapter Four - Monte Carlo and Molecular Dynamics*, in *Adsorption by Carbons*. 2008, Elsevier: Amsterdam. p. 77-101.
- [94] Horikawa, T.;Zeng, Y.;Do, D.D.;Sotowa, K.;Alcantara Avila, J.R., *On the isosteric heat of adsorption of non-polar and polar fluids on highly graphitized carbon black.* J Colloid Interface Sci, 2015. **439**: p. 1-6.
- [95] Zachariasen, W.H., *The atomic arrangement in glass.* Journal of the American Chemical Society, 1932. **54**: p. 3841-3851.
- [96] Zhuravlev, L.T., *The surface chemistry of amorphous silica. Zhuravlev model.* Colloids and Surfaces a-Physicochemical and Engineering Aspects, 2000. **173**(1-3): p. 1-38.
- [97] Wooten, F.;Winer, K.;Weaire, D., *Computer-Generation of Structural Models of Amorphous Si and Ge.* Physical Review Letters, 1985. **54**(13): p. 1392-1395.

- [98] Barkema, G.T.;Mousseau, N., *High-quality continuous random networks*. Physical Review B, 2000. **62**(8): p. 4985-4990.
- [99] McGreevy, R.L., *Reverse Monte Carlo modelling*. Journal of Physics-Condensed Matter, 2001. **13**(46): p. R877-R913.
- [100] Muller, C.R.;Kathiraratchi, V.;Schuch, M.;Maass, P.;Petkov, V.G., *Reverse Monte Carlo modeling of ion conducting network glasses: An evaluation based on molecular dynamics simulations*. Physical Chemistry Chemical Physics, 2010. **12**(35): p. 10444-10451.
- [101] Biswas, P.;Atta-Fynn, R.;Drabold, D.A., *Reverse Monte Carlo modeling of amorphous silicon*. Physical Review B, 2004. **69**(19).
- [102] Peng, L.;Qisui, W.;Xi, L.;Chaocan, Z., *Investigation of the states of water and OH groups on the surface of silica*. Colloids and Surfaces a-Physicochemical and Engineering Aspects, 2009. **334**(1-3): p. 112-115.
- [103] Leed, E.A.;Pantano, C.G., *Computer modeling of water adsorption on silica and silicate glass fracture surfaces*. Journal of Non-Crystalline Solids, 2003. **325**(1-3): p. 48-60.
- [104] Liu, J.;LeVan, M.D., *Henry's law constants and isosteric heats of adsorption at zero loading for multi-wall carbon surfaces with different geometries*. Carbon, 2010. **48**(12): p. 3454-3462.
- [105] Steele, W.A., *The interaction of gases with solid surfaces*. 1st ed. The International encyclopedia of physical chemistry and chemical physics Topic 14: Properties of interfaces,. 1974, Oxford ; New York: Pergamon Press. xi, 349 p.
- [106] Ionov, S.I.;LaVilla, M.E., *Probing the molecule-surface interaction via inversion symmetry changes in the scattering of state - selected ND₃ on graphite (0001)*. The Journal of Chemical Physics, 1992. **97**(12): p. 9379-9388.

- [107] Buckingham, A.D., *Permanent and Induced Molecular Moments and Long-Range Intermolecular Forces*. Advances in Chemical Physics, 1967. **12**: p. 107-142.
- [108] Jorgensen, W.L.;Chandrasekhar, J.;Madura, J.D.;Impey, R.W.;Klein, M.L., *Comparison of Simple Potential Functions for Simulating Liquid Water*. Journal of Chemical Physics, 1983. **79**(2): p. 926-935.
- [109] Petkov, V.;Billinge, S.J.L.;Shastri, S.D.;Himmel, B., *Polyhedral units and network connectivity in calcium aluminosilicate glasses from high-energy X-ray diffraction*. Physical Review Letters, 2000. **85**(16): p. 3436-3439.
- [110] Le Roux, S.;Petkov, V., *ISAACS - interactive structure analysis of amorphous and crystalline systems*. Journal of Applied Crystallography, 2010. **43**: p. 181-185.
- [111] Hoang, V.V., *Molecular dynamics simulation of amorphous SiO₂ nanoparticles*. J Phys Chem B, 2007. **111**(44): p. 12649-56.
- [112] Kohara, S.;Suzuya, K., *Intermediate-range order in vitreous SiO₂ and GeO₂*. Journal of Physics-Condensed Matter, 2005. **17**(5): p. S77-S86.
- [113] Cruz-Chu, E.R.;Aksimentiev, A.;Schulten, K., *Water-silica force field for simulating nanodevices*. J Phys Chem B, 2006. **110**(43): p. 21497-508.
- [114] Lakhliifi, A.;Killingbeck, J.P., *Dynamic and spectroscopic studies of single molecules physisorbed on graphite substrates. 2. Application to the ammonia molecule*. Journal of Physical Chemistry B, 2005. **109**(22): p. 11322-11331.
- [115] Kakiuchi, H.;Shimooka, S.;Iwade, M.;Oshima, K.;Yamazaki, M.;Terada, S.;Watanabe, H.;Takewaki, T., *Novel Water Vapor Adsorbent FAM-Z01 and its Applicability to an Adsorption Heat Pump*. KAGAKU KOGAKU RONBUNSHU, 2005. **31**(5): p. 361-364.

- [116] Shimooka, S.;Oshima, K.;Hidaka, H.;Takewaki, T.;Kakiuchi, H.;Kodama, A.;Kubota, M.;Matsuda, H., *The Evaluation of Direct Cooling and Heating Desiccant Device Coated with FAM*. JOURNAL OF CHEMICAL ENGINEERING OF JAPAN, 2007. **40**(13): p. 1330-1334.
- [117] Kakiuchi, H.;Shimooka, S.;Iwade, M.;Oshima, K.;Yamazaki, M.;Terada, S.;Watanabe, H.;Takewaki, T., *Water Vapor Adsorbent FAM-Z02 and Its Applicability to Adsorption Heat Pump*. KAGAKU KOGAKU RONBUNSHU, 2005. **31**(4): p. 273-277.
- [118] Everett, D.H.;Powl, J.C., *Adsorption in slit-like and cylindrical micropores in the henry's law region. A model for the microporosity of carbons*. Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, 1976. **72**(0): p. 619-636.
- [119] Savitz, S.;Siperstein, F.;Gorte, R.J.;Myers, A.L., *Calorimetric Study of Adsorption of Alkanes in High-Silica Zeolites*. The Journal of Physical Chemistry B, 1998. **102**(35): p. 6865-6872.
- [120] Lobo, R.F., *Chapter 9 - Intermolecular Forces in Zeolite Adsorption and Catalysis*, in *Ordered Porous Solids*. 2009, Elsevier: Amsterdam. p. 239-261.
- [121] Rappe, A.K.;Casewit, C.J.;Colwell, K.S.;Goddard, W.A.;Skiff, W.M., *Uff, a Full Periodic-Table Force-Field for Molecular Mechanics and Molecular-Dynamics Simulations*. Journal of the American Chemical Society, 1992. **114**(25): p. 10024-10035.
- [122] Faro, T.M.C.;Thim, G.P.;Skaf, M.S., *A Lennard-Jones plus Coulomb potential for Al³⁺ ions in aqueous solutions*. The Journal of Chemical Physics, 2010. **132**(11): p. 114509.
- [123] Jiang, J.-W.;Park, H.S., *A Gaussian treatment for the friction issue of Lennard-Jones potential in layered materials: Application to friction between graphene, MoS₂, and black phosphorus*. Journal of Applied Physics, 2015. **117**(12): p. 124304.

- [124] Kusalik, P.G.;Svishchev, I.M., *The Spatial Structure in Liquid Water*. Science, 1994. **265**(5176): p. 1219-1221.
- [125] Steele, W.A., *Physical Interaction of Gases with Crystalline Solids .1. Gas-Solid Energies and Properties of Isolated Adsorbed Atoms*. Surface Science, 1973. **36**(1): p. 317-352.
- [126] Abascal, J.L.F.;Vega, C., *The water forcefield: Importance of dipolar and quadrupolar interactions*. Journal of Physical Chemistry C, 2007. **111**(43): p. 15811-15822.
- [127] Hansen, F.Y.;Bruch, L.W.;Roosevelt, S.E., *Electrostatic Forces and the Frequency-Spectrum of a Monolayer Solid of Linear-Molecules on Graphite*. Physical Review B, 1992. **45**(19): p. 11238-11248.
- [128] Vidali, G.;Cole, M.W., *Lateral Variation of the Physisorption Potential for Noble-Gases on Graphite*. Physical Review B, 1984. **29**(12): p. 6736-6738.
- [129] Spassova, M.;Monev, V.;Kanev, I.;Champagne, B.;Mosley, D.H.;J.M., A., *Ab Initio Summation Over States/SCI for Static and Dynamic Hyperpolarizabilities of Small Molecules*. Quantum Systems in Chemistry and Physics, ed. al, H.-L.e. Vol. Basic Problems and Model Systems. 2000, Great Britain: Kluwer Academic Publishers.
- [130] Chelli, R.;Pagliai, M.;Procacci, P.;Cardini, G.;Schettino, V., *Polarization response of water and methanol investigated by a polarizable force field and density functional theory calculations: Implications for charge transfer*. Journal of Chemical Physics, 2005. **122**(7).
- [131] DiStasio, R.A.;Gobre, V.V.;Tkatchenko, A., *Many-body van der Waals interactions in molecules and condensed matter*. Journal of Physics: Condensed Matter, 2014. **26**(21).
- [132] Avgul, N.N.;Kieslev, A.V., *Chemistry and Physics of Carbon*, ed. Walker, P.L. 1970, New York: Marcel Dekker.

- [133] Markovic, N.;Andersson, P.U.;Nagard, M.B.;Pettersson, J.B.C., *Scattering of water from graphite: simulations and experiments*. Chemical Physics, 1999. **247**(3): p. 413-430.
- [134] Lin, C.S.;Zhang, R.Q.;Lee, S.T.;Elstner, M.;Frauenheim, T.;Wan, L.J., *Simulation of water cluster assembly on a graphite surface*. Journal of Physical Chemistry B, 2005. **109**(29): p. 14183-14188.
- [135] Rubeš, M.;Nachtigall, P.;Vondrášek, J.;Bludský, O., *Structure and Stability of the Water–Graphite Complexes*. The Journal of Physical Chemistry C, 2009. **113**(19): p. 8412-8419.
- [136] Feller, D.;Jordan, K.D., *Estimating the strength of the water/single-layer graphite interaction*. Journal of Physical Chemistry A, 2000. **104**(44): p. 9971-9975.
- [137] Pertsin, A.;Grunze, M., *Water-graphite interaction and behavior of water near the graphite surface*. Journal of Physical Chemistry B, 2004. **108**(4): p. 1357-1364.
- [138] Liu, J.C.;Monson, P.A., *Monte Carlo simulation study of water adsorption in activated carbon*. Industrial and Engineering Chemistry Research, 2006. **45**(16): p. 5649-5656.
- [139] Karapetian, K.;Jordan, K.D., *Water in Confined Environments*, ed. Devlin, J.P.;Buch, V. 2003, New York: Springer.
- [140] Sanfelix, P.C.;Holloway, S.;Kolasinski, K.W.;Darling, G.R., *The structure of water on the (0001) surface of graphite*. Surface Science, 2003. **532**: p. 166-172.
- [141] Karlicky, F.;Otyepkova, E.;Banas, P.;Lazar, P.;Kocman, M.;Otyepka, M., *Interplay between Ethanol Adsorption to High-Energy Sites and Clustering on Graphene and Graphite Alters the Measured Isosteric Adsorption Enthalpies*. Journal of Physical Chemistry C, 2015. **119**(35): p. 20535-20543.

- [142] Chua, H.T.;Ng, K.C.;Chakraborty, A.;Oo, N.M.;Othman, M.A., *Adsorption characteristics of silica gel plus water systems*. Journal of Chemical and Engineering Data, 2002. **47**(5): p. 1177-1181.
- [143] Chakraborty, A.;Saha, B.B.;Koyama, S.;Ng, K.C.;Srinivasan, K., *Adsorption Thermodynamics of Silica Gel-Water Systems*. Journal of Chemical and Engineering Data, 2009. **54**(2): p. 448-452.
- [144] Lemmon, E.W.;Huber, M.L.;McLinden.M.O., *NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 8.0*, Program, S.R.D., Editor. 2007, National Institute of Standards and Technology: Gaithersburg.
- [145] Tóth, J., *Thermodynamical Correctness of Gas/Solid Adsorption Isotherm Equations*. Journal of Colloid and Interface Science, 1994. **163**(2): p. 299-302.
- [146] McEnaney, B., *Estimation of the dimensions of micropores in active carbons using the Dubinin-Radushkevich equation*. Carbon, 1987. **25**(1): p. 69-75.
- [147] NACC, *PTX data for silica gel/water pair, Manufacturer's Proprietary Data*. Nishiyodo Air Conditioning Co Ltd.Tokyo, Japan, 1992.
- [148] Khalfaoui, M.;Knani, S.;Hachicha, M.A.;Lamine, A.B., *New theoretical expressions for the five adsorption type isotherms classified by BET based on statistical physics treatment*. Journal of Colloid and Interface Science, 2003. **263**(2): p. 350-356.
- [149] Chakraborty, A.;Saha, B.B.;Ng, K.C.;Koyama, S.;Srinivasan, K., *Theoretical insight of physical adsorption for a single-component adsorbent+adsorbate system: I. Thermodynamic property surfaces*. Langmuir, 2009. **25**(4): p. 2204-11.

- [150] Critoph, R.E.;Metcalf, S.J., *Specific cooling power intensification limits in ammonia–carbon adsorption refrigeration systems*. Applied Thermal Engineering, 2004. **24**(5-6): p. 661-678.
- [151] Ravikovitch, P.I.;Vishnyakov, A.;Neimark, A.V., *Density functional theories and molecular simulations of adsorption and phase transitions in nanopores*. Physical Review E, 2001. **64**(1).
- [152] Ribeiro, R.P.;Sauer, T.P.;Lopes, F.V.;Moreira, R.F.;Grande, C.A.;Rodrigues, A.r.E., *Adsorption of CO₂, CH₄, and N₂ in Activated Carbon Honeycomb Monolith*. Journal of Chemical & Engineering Data, 2008. **53**(10): p. 2311-2317.
- [153] Mclean, A.D.;Yoshimine, M., *Higher Polarizabilities of Linear Molecules*. Journal of Chemical Physics, 1967. **46**(9): p. 3682-+.
- [154] Norman, G.E.;Filinov, V.S., *Investigations of Phase Transitions by a Monte-Carlo Method*. High Temperature, 1969. **7**(2): p. 216-&.
- [155] Amar, J.G., *The Monte Carlo method in science and engineering*. Computing in Science & Engineering, 2006. **8**(2): p. 9-19.
- [156] Smykowski, D.;Szyja, B.;Szczygieł, J., *GCMC simulations of CO₂ adsorption on zeolite-supported Ir₄ clusters*. Journal of Molecular Graphics and Modelling, 2014. **50**: p. 35-43.
- [157] Cheng, J.R.;Yuan, X.H.;Zhao, L.;Huang, D.C.;Zhao, M.;Dai, L.;Ding, R., *GCMC simulation of hydrogen physisorption on carbon nanotubes and nanotube arrays*. Carbon, 2004. **42**(10): p. 2019-2024.
- [158] Mahdizadeh, S.J.;Goharshadi, E.K., *Hydrogen storage on silicon, carbon, and silicon carbide nanotubes: A combined quantum mechanics and grand canonical Monte Carlo simulation study*. International Journal of Hydrogen Energy, 2014. **39**(4): p. 1719-1731.

- [159] Wu, Y.;Chen, H.Y.;Liu, D.F.;Qian, Y.;Xi, H.X., *Adsorption and separation of ethane/ethylene on ZIFs with various topologies: Combining GCMC simulation with the ideal adsorbed solution theory (IAST)*. Chemical Engineering Science, 2015. **124**: p. 144-153.

Appendices

A. Computational Strategy

A1. Multipole Expansion of Energy

The energy of uncharged molecule in static electric field can be expressed by multipole expansion formulation [1, 2],

$$\begin{aligned} U = U^0 &- \boldsymbol{\mu}_\alpha \mathbf{F}_\alpha - \frac{1}{3} \boldsymbol{\Theta}_{\alpha\beta} \mathbf{F}_\alpha \mathbf{F}_\beta - \frac{1}{15} \boldsymbol{\Omega}_{\alpha\beta\gamma} \mathbf{F}_\alpha \mathbf{F}_\beta \mathbf{F}_\gamma - \frac{1}{105} \boldsymbol{\Phi}_{\alpha\beta\gamma\delta} \mathbf{F}_\alpha \mathbf{F}_\beta \mathbf{F}_\gamma \mathbf{F}_\delta + \dots \\ &- \frac{1}{2} \boldsymbol{\alpha}_{\alpha\beta} \mathbf{F}_\alpha \mathbf{F}_\beta - \frac{1}{3} \mathbf{A}_{\alpha,\beta\gamma} \mathbf{F}_\alpha \mathbf{F}_\beta \mathbf{F}_\gamma - \frac{1}{6} \mathbf{C}_{\alpha\beta,\gamma\delta} \mathbf{F}_\alpha \mathbf{F}_\beta \mathbf{F}_\gamma \mathbf{F}_\delta - \frac{1}{15} \mathbf{E}_{\alpha,\beta\gamma\delta} \mathbf{F}_\alpha \mathbf{F}_\beta \mathbf{F}_\gamma \mathbf{F}_\delta + \dots \\ &- \frac{1}{6} \boldsymbol{\beta}_{\alpha\beta\gamma} \mathbf{F}_\alpha \mathbf{F}_\beta \mathbf{F}_\gamma - \frac{1}{6} \mathbf{B}_{\alpha\beta,\gamma\delta} \mathbf{F}_\alpha \mathbf{F}_\beta \mathbf{F}_\gamma \mathbf{F}_\delta + \dots \\ &- \frac{1}{24} \boldsymbol{\gamma}_{\alpha\beta\gamma\delta} \mathbf{F}_\alpha \mathbf{F}_\beta \mathbf{F}_\gamma \mathbf{F}_\delta + \dots, \end{aligned} \quad (\text{A1})$$

where U^0 is the energy of free molecule, $\boldsymbol{\mu}_\alpha$, $\boldsymbol{\Theta}_{\alpha\beta}$, $\boldsymbol{\Omega}_{\alpha\beta\gamma}$ and $\boldsymbol{\Phi}_{\alpha\beta\gamma\delta}$ are dipole, quadrupole, octupole and hexadecapole moment, $\boldsymbol{\alpha}_{\alpha\beta}$, $\boldsymbol{\beta}_{\alpha\beta\gamma}$ and $\boldsymbol{\gamma}_{\alpha\beta\gamma\delta}$ are dipole polarizabilities, $\mathbf{A}_{\alpha,\beta\gamma}$, $\mathbf{C}_{\alpha\beta,\gamma\delta}$, $\mathbf{E}_{\alpha,\beta\gamma\delta}$ and $\mathbf{B}_{\alpha\beta,\gamma\delta}$ are the quadrupole polarizabilities, $\mathbf{F}$ with subscripts are electric field, electric field gradient (EFG), etc. depends on the number of groups of subscripts. By applying the specific reduction strategies on equation (4.5) based on the multipole properties of the molecule [3], the multipole expression is suitable for the calculation of interaction energy of molecules.

A2. Reduced Multipole Expansion of Energy

Taking Lennard-Jones (LJ) and quadrupole-quadrupole interaction into consideration, Pople [4] modified the potential and is given by,

$$U = u_{\text{LJ}} + u_{\text{quadrupole-quadrupole}} \quad (\text{A2})$$

Considering **Keesom Force** between dipolar molecules, Keesom [5] also proposed the improved intermolecular potential model as

$$U = U_{\text{HS}} + U_{\text{dipole-dipole}} \text{ or } U = U_{\text{HS}} + U_{\text{quadrupole-quadrupole}} \quad (\text{A3})$$

For non-polar molecules, the interaction potential can be expressed by LJ potential sufficiently while electrostatic and induction effect cannot be neglected for polar molecules. Therefore, by combining the Lenard-Jones, electrostatic and induction potential U_{LJ} , U_{E} , U_{I} , the total interaction potential U_{mM} is proposed to obtain more complete description of interaction potential for polar molecules.

$$U_{\text{mM}} = U_{\text{LJ}} + U_{\text{E}} + U_{\text{I}} \quad (\text{A4})$$

A3. Electric Field and Energy of multipole

Potential of dipole in static electric field

The potential of permanent dipole in electric field $\mathbf{F}$ is,

$$U = -\boldsymbol{\mu} \cdot \mathbf{F} \quad (\text{A5})$$

A permanent dipole placed in static electric field will induce a temporary dipole with the same dipole moment and opposite direction. In the non-linear regime, the induced dipole moment $\boldsymbol{\mu}^{\text{I}}$ is,

$$\boldsymbol{\mu}^{\text{I}} = \boldsymbol{\alpha} \cdot \mathbf{F}, \quad (\text{A6})$$

where $\boldsymbol{\alpha}$ is the dipole moment polarizability tensor of an acceptor of electric field and $\mathbf{F}$ is the exerted static electric field. Due to the induced dipole instead of a permanent one, the induction potential U_{I} is,

$$U_{\text{I}} = -\frac{1}{2} \boldsymbol{\mu}^{\text{I}} \cdot \mathbf{F} \quad (\text{A7})$$

The **Debye Force** between dipole and induced dipole adds to the intermolecular potential when non-zero dipole moment exists in the interaction pair. Taking this **Induction Effect** into account, the interaction potential U_{I} is,

$$U = U_I = -\frac{1}{2} \boldsymbol{\alpha} \cdot \mathbf{F}^2 \quad (\text{A8})$$

Electric field generated by a dipole

Generally, the applied approximate equation for electric potential is valid for large distance. The dipole moment of water molecule is $p = 1.85 \text{ D}$ and the equivalent displacement is $d = p/q = 1.85 \times (3.33564 \times 10^{-30} \text{ C} \cdot \text{m}) / (0.82 \times 1.6 \times 10^{-19} \text{ C}) = 4.7 \times 10^{-11} \text{ m} = 0.47 \text{ \AA}$ given that $qO = -0.82e$. In the calculation of interaction potential for water, the cut-off distance of $z=2.5 \text{ \AA}$, which is more than 5 times of the displacement of the dipole. Therefore, the expression used for electric potential of dipole moment is considered as an acceptable approximation even for the minimum separation. Meanwhile, the accuracy of the expression will increase as the adsorbate-adsorbent separation z increases because the error of this approximation is inverse proportional to z^2 , which means the rest $U(z)$ values on the potential curves are more reliable than the acceptable $U(z_{\text{cut-off}})$ [6]. Lastly, the final result reveals the fact that even for polar molecules the LJ potential is still the dominant part in the interaction potential and this also moderates the approximation of electric potential expressions. The electric potential of elementary charge in the electric field excited by a permanent dipole $\boldsymbol{\mu}$ at the distance $\mathbf{r}$ is,

$$\Phi_{\text{dipole}}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \frac{\mathbf{r} \cdot \boldsymbol{\mu}}{r^3} \quad (\text{A9})$$

The electric field excited by a permanent dipole $\boldsymbol{\mu}$ at the distance $\mathbf{r}$ is,

$$\mathbf{E}_{\text{dipole}}(\mathbf{r}) = -\nabla\Phi_{\text{dipole}}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \left(\frac{3(\boldsymbol{\mu} \cdot \mathbf{r})\mathbf{r}}{r^5} - \frac{\boldsymbol{\mu}}{r^3} \right) \quad (\text{A10})$$

Potential of quadrupole in static electric field

The potential of a quadrupole in electric field $\mathbf{F}$ is the double point product of two tensors,

$$U = -\frac{1}{3} \boldsymbol{\Theta} : \nabla \mathbf{F}, \quad (\text{A11})$$

where Θ is the quadrupole moment tensor and $\nabla\mathbf{F}$ is the EFG tensor.

Electric field generated by a quadrupole

The electric potential of elementary charge in the electric field excited by a quadrupole Θ at the distance $\mathbf{r}$ is,

$$\phi_{\text{quadrupole}}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \frac{1}{2} \frac{\mathbf{r}^T \cdot \Theta \cdot \mathbf{r}}{\mathbf{r}^5} \quad (\text{A12})$$

The electric field excited by a quadrupole Θ at the distance $\mathbf{r}$ is,

$$\mathbf{E}_{\text{quadrupole}}(\mathbf{r}) = -\nabla\phi_{\text{quadrupole}}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \left(\frac{(5\mathbf{r}^T \cdot \Theta \cdot \mathbf{r})\mathbf{r}}{2\mathbf{r}^7} - \frac{\Theta \cdot \mathbf{r}}{\mathbf{r}^5} \right) \quad (\text{A13})$$

The EFG tensor of quadrupole Θ at the distance $\mathbf{r}$ is

$$\mathbf{EFG}(\mathbf{r}) = \nabla\mathbf{E}_{\text{quadrupole}}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \left(\frac{(5\mathbf{r}^T \cdot \Theta \cdot \mathbf{r})\mathbf{I}}{2\mathbf{r}^7} + \frac{\Theta}{\mathbf{r}^5} \right) \quad (\text{A14})$$

where $\mathbf{r}^T$ is the transposed position vector, $\mathbf{I}$ is a 3×3 unit diagonal matrix.

A4. Computational Strategy

The computational strategy for electric field generated by both molecules of this simulation is shown in **Table A1**

Table 4A1 The computation of electric field with induction effect for a pair of molecules

Step 0: Initiate electric fields

$$\mathbf{E}_m(-\mathbf{r}) = \mathbf{E}_m^0(-\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \left(\frac{\boldsymbol{\mu}_m}{r^3} - \frac{3(\boldsymbol{\mu}_m \cdot \mathbf{r})\mathbf{r}}{r^5} \right) + \frac{1}{4\pi\epsilon_0} \left(\frac{(5\mathbf{r}^T \cdot \boldsymbol{\Theta}_m \cdot \mathbf{r})\mathbf{r}}{2r^7} - \frac{\boldsymbol{\Theta}_m \cdot \mathbf{r}}{r^5} \right)$$

$$\mathbf{E}_M(\mathbf{r}) = \mathbf{E}_M^0(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \left(\frac{(5\mathbf{r}^T \cdot \boldsymbol{\Theta}_M \cdot \mathbf{r})\mathbf{r}}{2r^7} - \frac{\boldsymbol{\Theta}_M \cdot \mathbf{r}}{r^5} \right)$$

$$\mathbf{E}_m^I(-\mathbf{r}) = [\mathbf{E}_m^I(-\mathbf{r})]^0 = 0$$

$$\mathbf{E}_M^I(\mathbf{r}) = [\mathbf{E}_M^I(\mathbf{r})]^0 = 0$$

$$i = 1$$

Step 1: Update electric fields

$$\mathbf{E}_m^i(-\mathbf{r}) = \mathbf{E}_m^0(-\mathbf{r}) + \mathbf{E}_m^I(-\mathbf{r})$$

$$\mathbf{E}_M^i(\mathbf{r}) = \mathbf{E}_M^0(\mathbf{r}) + \mathbf{E}_M^I(\mathbf{r})$$

Step2: Calculate induced dipoles

$$\boldsymbol{\mu}_m^I = \boldsymbol{\alpha}_m \cdot \mathbf{E}_M^i(\mathbf{r})$$

$$\boldsymbol{\mu}_M^I = \boldsymbol{\alpha}_M \cdot \mathbf{E}_m^i(-\mathbf{r})$$

Step3: Update electric fields of induced dipoles

$$\mathbf{E}_m^I(-\mathbf{r}) = [\mathbf{E}_m^I(-\mathbf{r})]^i = \frac{1}{4\pi\epsilon_0} \left(\frac{\boldsymbol{\mu}_m^I}{r^3} - \frac{3(\boldsymbol{\mu}_m^I \cdot \mathbf{r})\mathbf{r}}{r^5} \right)$$

$$\mathbf{E}_M^I(\mathbf{r}) = [\mathbf{E}_M^I(\mathbf{r})]^i = \frac{1}{4\pi\epsilon_0} \left(\frac{3(\boldsymbol{\mu}_M^I \cdot \mathbf{r})\mathbf{r}}{r^5} - \frac{\boldsymbol{\mu}_M^I}{r^3} \right)$$

Step 4: Iteration*

$$\text{if } (|\mathbf{E}_m^i(-\mathbf{r}) - \mathbf{E}_m^{i-1}(-\mathbf{r})|/|\mathbf{E}_m^{i-1}(-\mathbf{r})| < \mathbf{e} \text{ and } |\mathbf{E}_M^i(\mathbf{r}) - \mathbf{E}_M^{i-1}(\mathbf{r})|/|\mathbf{E}_M^{i-1}(\mathbf{r})| < \mathbf{e})$$

Stop computation

else

$i = i + 1$ and Go to **Step 1**

*The total number of iterations can be defined to stop the computation as long as the difference of electric field calculated in two consecutive iterations satisfies the convergence criterion $\mathbf{e}$.

The sum of electric field of all pairs of the adsorbate and adsorbent molecules can be used to calculate the induction potential of the whole system.

The computational strategy for interaction potential of one adsorbate molecule and the multilayers of carbon atoms is shown in **Table A2**

Table A2 The computation of interaction potential of one adsorbate molecule and multilayer carbon atoms

Step 0: Initiate position and orientation of adsorbate molecule

$$\mathbf{r}_M = \mathbf{T}_{\alpha,\beta,\gamma} \mathbf{r}_m + \mathbf{r}_{m,0} *$$

$$U_{mM} = U_{LJ}^0 = U_E^0 = U_I^0 = 0$$

$$i = 1$$

Step 1: Update electric field, EFG and induced dipole moment

Update $\mathbf{E}_m^i(-\mathbf{r}_M)$, $\mathbf{E}_M^i(\mathbf{r}_M)$, $\boldsymbol{\mu}_m^I$ and $\boldsymbol{\mu}_M^I$ according to Table 1

$$\mathbf{EFG}_M^i(\mathbf{r}_M) = \frac{1}{4\pi\epsilon_0} \left(\frac{(5\mathbf{r}_M^T \cdot \boldsymbol{\Theta} \cdot \mathbf{r}_M) \mathbf{I}}{2r_M^7} + \frac{\boldsymbol{\Theta}}{r_M^5} \right)$$

Step2: Calculate interaction potential

$$U_{LJ}^i = U_{LJ}^{i-1} + \sum U_{LJ}(\mathbf{r}_M) **$$

$$U_E^i = U_E^{i-1} + \boldsymbol{\mu}_m \mathbf{E}_M^i(\mathbf{r}_M) + \frac{1}{3} \boldsymbol{\Theta}_m : \mathbf{EFG}_M^i(\mathbf{r}_M)$$

$$U_I^i = U_I^{i-1} - \frac{1}{2} \boldsymbol{\mu}_m^I \mathbf{E}_M^i(\mathbf{r}_M) - \frac{1}{2} \boldsymbol{\mu}_M^I \mathbf{E}_m^i(-\mathbf{r}_M)$$

Step 3: Iteration until I reaches the total number of carbon atoms

if ($i > N$)

$$U_{mM} = U_{LJ}^N + U_E^N + U_I^N$$

Stop computation

else

$i = i + 1$ and Go to **Step 1**

* See **9. Coordinate transformation**

**eq (4.1) in main text is applied to each atom of adsorbate molecule with corresponding position vectors and the sum will be the LJ part of interaction potential between one adsorbate molecule and one carbon atom.

The computational strategy for isosteric heat of adsorption at zero surface coverage is shown in

Table A3

Table A3 The computation of isosteric heat of adsorption at zero surface coverage

<p>Step 0: Initialize constant and parameters</p> <p>k_B, T, integration method and precision, etc</p> <p>Step 1: Initialize interaction potential function*</p> $U_{mM}(z) = U_{mM}(\mathbf{r}(z)) _{x_0, y_0} = U_{mM}(x_0, y_0, z)$ $U_{mM}(H - z) = U_{mM}(\mathbf{r}(H - z)) _{x_0, y_0} = U_{mM}(x_0, y_0, H - z)$ <p>Step 2: Initialize external wall potential</p> $V_{ext}(z) = U_{mM}(z) + U_{mM}(H - z) = U_{mM}(x_0, y_0, z) + U_{mM}(x_0, y_0, H - z)$ <p>Step 3: Integrate for numerator</p> $f_{nume}(H) = \int_0^H V_{ext}(z) e^{-\frac{V_{ext}(z)}{k_B T}} dz$ <p>Step 4: Integrate for denominator</p> $f_{denomi}(H) = \int_0^H e^{-\frac{V_{ext}(z)}{k_B T}} dz$ <p>Step 5: Calculate isosteric heat of adsorption</p> $q_{st}^o(H) = k_B T - \frac{\int_0^H V_{ext}(z) e^{-\frac{V_{ext}(z)}{k_B T}} dz}{\int_0^H e^{-\frac{V_{ext}(z)}{k_B T}} dz} = k_B T - \frac{f_{nume}(H)}{f_{denomi}(H)}$ <p>Stop computation.</p>
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* The interaction potential as a function of separation distance z is obtained by interpolation method from simulation data provided in **Table A2**

A5. Dipole-quadrupole Interaction Potential

Non-zero dipole and quadrupole moment exists in the interaction pair of molecule (denoted by $\mathbf{m}$ and $\mathbf{M}$, respectively), the dipole-quadrupole interaction needs to be taken into consideration in

the calculation of interaction potential. The interaction effect may decompose into three steps, i.e.,

firstly, the generation of electric field by the dipole and quadrupole,

secondly, the deriving of interaction potential of dipole and quadrupole in the generated static electric field (electrostatic potential),

thirdly, the deriving of interaction potential of induced dipole in the generated static electric field (induction potential).

Therefore, the dipole-quadrupole interaction consist of electrostatic potential u_E and induction potential u_I . The electrostatic potential is,

$$\begin{aligned} U_E &= U_{\text{dipole},E(\text{quarupole} \rightarrow \text{dipole})} + U_{\text{quadrupole},E(\text{dipole} \rightarrow \text{quarupole})} \\ &= \boldsymbol{\mu}_m \cdot \mathbf{E}_M(\mathbf{r}) + \frac{1}{3} \boldsymbol{\Theta}_m \cdot \nabla \mathbf{E}_M(\mathbf{r}), \end{aligned} \quad (\text{A15})$$

where $\mathbf{r}$ is the distance vector from quadrupole to dipole, $\mathbf{E}_M(\mathbf{r})$ is the electric filed at the dipole generated by the quadrupole, $\nabla \mathbf{E}_M(\mathbf{r})$ is the **EFG** of $\mathbf{E}_M(\mathbf{r})$. Considering that the molecule M with only non-zero quadrupole moment can still induce dipole in static electric field, both induction effects should be added to the total induction potential during deriving U_I . The induction potential is

$$\begin{aligned} U_I &= U_{\text{dipole},E(\text{quarupole} \rightarrow \text{dipole})}^I + U_{\text{quadrupole},E(\text{dipole} \rightarrow \text{quarupole})}^I \\ &= -\frac{1}{2} \boldsymbol{\alpha}_m \cdot \mathbf{E}_M^2(\mathbf{r}) - \frac{1}{2} \boldsymbol{\alpha}_M \cdot \mathbf{E}_m^2(-\mathbf{r}) \end{aligned} \quad (\text{A16})$$

where $\boldsymbol{\alpha}_m$ is the dipole polarizability of the molecule with non-zero dipole moment $\boldsymbol{\mu}$, $\boldsymbol{\alpha}_M$ is the dipole polarizability of the molecules with non-zero quadrupole moment $\boldsymbol{\Theta}$. In consideration of the contribution of electric field generated by the induced dipole on molecules, the electric field at $\mathbf{r}$ and $-\mathbf{r}$ should be calculated iteratively.

A6. Interaction Potential of Water on Graphite

With fixed z , the interaction potential can vary with x and y because of the change of relative orientation of adsorbate molecule to the centre of hexagonal unit cell of graphite lattice. The distribution of interaction potential of water on graphite at orientation 1 to 5 in the simulated space is plotted as Figures A1(a) to A1(e). Six blue points represent the position of carbon atoms of hexagonal unit cell on XY plane.

Figure A1(a) Interaction potential of water on graphite at orientation 1 and $Z=3\text{\AA}$.

Figure A1(b) Interaction potential of water on graphite at orientation 2 and $Z=3.5\text{\AA}$.

Figure A1(c) Interaction potential of water on graphite at orientation 3 and $Z=3\text{\AA}$

Figure A1(d) Interaction potential of water on graphite at orientation 4 and $Z=3.5\text{\AA}$.

Figure A1(e) Interaction potential of water on graphite at orientation 5 and $Z=3\text{\AA}$.

For understanding the LJ, induction and electrostatic potentials, plots of interaction energy as a function of C $\cdots$ O separation distance for orientations 4 and 5 of a water molecule are shown in Figures A2(a) and A2(b).

Figure A2 Water potential plots for (a) orientation 4 (b) orientation 5 ($U_E > 0$ for orientation 4 and $U_E < 0$ for orientation 5)

A7. Interaction Potential of Methanol on Graphite

The distribution of interaction potential of methanol on graphite at orientations 1, 2 and 3 in the

Figure A3 Interaction potentials of methanol on graphite at (a) orientation 1 for $Z = 3.5$ Å, (b) orientation 2 and $Z = 3.5$ Å, and (c) orientation 3 and $Z = 3.5$ Å.

simulated space are plotted in Figures A3(a), A3(b) and A3(c) Six blue points represent the position of carbon atoms of hexagonal unit cell on XY plane.

For better understanding the LJ, induction and electrostatic potentials separately, a plot of interaction energy as a function of $C\cdots CH_3-OH$ separation distance for orientation 3 of methanol molecule is shown in Figure A4

Figure A4 Various interaction energy for methanol and graphite system at orientation 3

($U_E < 0$ for all of the 3 orientations)

A8. Interaction Potential of Ethanol on Graphite

The distribution of interaction potential of ethanol on graphite ranging from orientations 1 to 3 in the simulated space is plotted in Figures A5(a), A5(b) and A5(c) Six blue points represent the position of carbon atoms of hexagonal unit cell on XY plane.

The LJ, induction and electrostatic potentials are plotted as a function of $C\cdots CH_3-CH_2-OH$ separation distance for the orientation 2 of ethanol molecule is shown in Figure A6 It is observed that the electrostatic potential is very closed to zero and provides attractive force.

Figure A5 Interaction potential surface of ethanol on graphite for (a) orientation 1 (b) orientation 2 and (c) orientation 3 at $Z=3.5\text{\AA}$.

Figure A6 Ethanol potential for orientation 2 ($U_E < 0$ for all of the 3 orientations)

A9. Coordinate Transformation

For coordinate of atoms of adsorbate molecule, the coordinate transformation from the adsorbate coordinate system ($X'Y'Z'$) to the adsorbent (graphite) coordinate system (XYZ) can be accomplished by rotation and translation.

The column vector (x', y', z') in $X'Y'Z'$ system is rotated in the order of around X' , Y' and Z' axis by α , β and γ degree correspondingly. This temporary vector is then translated by a given translational vector (x_0, y_0, z_0) and the final column vector (x, y, z) is the transformation result from $X'Y'Z'$ system to XYZ system.

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} \cos \beta \cos \gamma & \cos \gamma \sin \alpha \sin \beta - \cos \alpha \sin \gamma & \cos \alpha \cos \gamma \sin \beta + \sin \alpha \sin \gamma \\ \cos \beta \sin \gamma & \sin \alpha \sin \beta \sin \gamma + \cos \alpha \cos \gamma & \cos \alpha \sin \beta \sin \gamma - \cos \gamma \sin \alpha \\ -\sin \beta & \cos \beta \sin \alpha & \cos \alpha \cos \beta \end{bmatrix} \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} + \begin{bmatrix} x_0 \\ y_0 \\ z_0 \end{bmatrix}$$

By combining various rotational angles and translational vectors, the coordinate of atoms of adsorbate molecules in any angle and distance to adsorbent molecules can be obtained.

References

- [1] A. D. Buckingham. Permanent and Induced Molecular Moments and Long-Range Intermolecular Forces. *Advances in Chemical Physics*. 1967, **12**: p.107-142.
- [2] A. D. McLean, M. Yoshimine. Higher Polarizabilities of Linear Molecules. *The Journal of Chemical Physics*. 1967, **46**: p.3682-3683.
- [3] George Maroulis, Constantinos Makris, Demetrios Xenides, Panagiotis Karamanis. Electric dipole and quadrupole moment and dipole polarizability of CS, SiO and SiS. *Molecular Physics*. 2000, **98**(8): p.481-491.
- [4] J. A. Pople. The Statistical Mechanics of Assemblies of Axially Symmetric Molecules. II. Second Virial Coefficients. *Proceedings of the Royal Society A: Mathematical, Physical & Engineering Sciences*. 1954, **221**: p.508-516.
- [5] A. D. Buckingham. Molecular quadrupole moments . *Quarterly Reviews, Chemical Society*. 1959, **13**: p.183-214.
- [6] D. J. Griffiths. *Introduction to Electrodynamics*. Prentice Hall.1999, 3rd Edition : 146.