

Hildebrand Solubility Parameters of Amidium Ionic Liquids

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ABSTRACT: The Hildebrand solubility parameters of amidium ionic liquids were investigated using the approach of intrinsic viscosity. It was discovered that the nature of the anion influences the Hildebrand solubility parameters by which distillable trifluoromethanesulfonate- (TfO⁻) based ionic liquids present higher Hildebrand solubility parameters than bis-(trifluoromethylsulfonyl)imide- (NTf₂⁻) based ionic liquids. In this work, we also studied the effect of dissolution temperature on the Hildebrand solubility parameters of ionic liquids. An increase in temperature from 25 to 60 °C results in a decrease in the Hildebrand solubility parameters of ionic liquids. Moreover, the cohesive energy density, molar internal energy, and enthalpy of dissolution were evaluated. The molar internal energy and enthalpy of dissolution are almost constant or show a slight decrease with increasing dissolution temperature for O-methylated TfO-based ionic liquids.

1. INTRODUCTION

In the past decade, ionic liquids, namely, salts that exist as liquids at relatively low temperatures below 100 °C, have attracted considerable attention in the scientific realm of electrochemical, catalytic, synthesis, and analytical chemistry applications.^{1–5} This is attributed to their numerous outstanding properties, including wide electrochemical windows, good thermal stability, high electrical conductivity, and designability.⁶ Having negligible vapor pressures, ionic liquids are potential alternatives to traditional volatile organic compounds. They are a promising class of environmentally friendly solvents that can enhance conventional processes, such as biomass pretreatment, drug delivery, and lubrication.^{7–9} Hence, understanding the solvation properties of ionic liquids is vital for the proper selection of solvents for different applications. The solvation powers of solvents are predicted by several approaches including the Abraham solvation model, Kamlet–Taft parameters, and Hildebrand solubility parameters.¹⁰ Among these approaches, solubility parameters, namely, numerical values that indicate the strength of molecular interactions between solvent molecules, have been widely used in many practical applications. The solubility parameter is a useful concept for selecting a suitable solvent for a solute, with solutes being miscible in solvents with similar solubility parameters.¹¹ Specifically, solubility parameters have been used to predict the compatibility of polymers, resins, and plasticizers; to prepare formulations of coatings; and to design pharmaceutical dosage forms.^{12,13}

The Hildebrand or total solubility parameter (δ_T) is defined as the square root of cohesive energy density (CED, the energy required to break the interactions between molecules)^{10,14}

$$\delta_T = (\text{CED})^{1/2} = \left(\frac{\Delta U}{V}\right)^{1/2} = \left(\frac{\Delta H - RT}{V}\right)^{1/2} \quad (1)$$

where V is the molar volume, ΔU is the molar internal energy, ΔH is the enthalpy of dissolution, R is the ideal gas constant, and T is the temperature. The Hildebrand solubility parameter can be evaluated by a variety of methods, namely, heat of vaporization–temperature data, group contribution methods, intrinsic viscosity, swelling values, turbidimetric titration, and

inverse gas chromatography.^{11,15} For nonvolatile compounds with extremely low vapor pressures, such as polymers, the solubility parameters cannot be determined by the heat of vaporization approach. In place of this method, the intrinsic viscosity method has been used extensively to determine the solubility parameters of these compounds.^{16,17}

The intrinsic viscosity approach involves the measurement of the intrinsic viscosity of a solute in a series of solvents to obtain the Hildebrand solubility parameter. The Hildebrand solubility parameter of the solute is equivalent to the Hildebrand solubility parameter of the solvent that gives the highest value of the solute's intrinsic viscosity.^{18,19} Thus, the intrinsic viscosity at its maximum indicates the maximum mutual compatibility between the solute and the solvent. This approach has been used to obtain the Hildebrand solubility parameters of solutes such as ionic liquids and (bio)polymers, and it has been marked as a fast, simple, and accurate method.^{19,20} Moreover, the intrinsic viscosity methodology shows good agreement with the values derived from different methods, such as the solvent dependence of the bimolecular rate constant of Diels–Alder reactions, computationally based techniques, and the activation energy of viscosity.^{19,21}

Recently, our group presented the synthesis of a novel class of low-cost amide-derived ionic liquids through amide O-alkylation with alkyl triflate. This case demonstrated the viability of facile recycling of aprotic ionic liquids through distillation of the regenerated molecular precursors at elevated temperatures without the need for further processing.²² Despite this important result, which can serve to address the recycling challenge of nonvolatile ionic liquids in large-scale applications, clearly more needs to be done to understand the physicochemical properties of this new class of distillable ionic liquids to select a promising ionic liquid for a particular application. Therefore, in this study, the Hildebrand solubility parameters of the novel class of distillable trifluoromethanesul-

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fonate- (TfO-) based ionic liquids were investigated by the reliable method of intrinsic viscosity. In addition, the Hildebrand solubility parameters of bis-(trifluoromethylsulfonyl)imide- (NTf₂-) based ionic liquids were determined to study the influence of ions on the Hildebrand solubility parameter. Moreover, in this study, we examined the effect of the dissolution temperature on the Hildebrand solubility parameter of the ionic liquid. In addition, further information on the cohesive energy density, molar internal energy, and enthalpy of dissolution were calculated from the Hildebrand solubility parameter, and the densities of the ionic liquids of interest were also determined.

2. EXPERIMENTAL SECTION

2.1. Chemicals. A series of O-alkylated amide-cation-based ionic liquids including O-methyl-diethylacetamidium triflate (MDEA-TfO), O-methyl-dimethylformamidium triflate (MDMF-TfO), O-methyl-N-ethylpyrrolidinonium triflate (MEPy-TfO), O-ethyl-diethylacetamidium triflate (EDEA-TfO), O-ethyl-dimethylacetamidium triflate (EDMA-TfO), O-ethyl-dimethylformamidium triflate (EDMF-TfO), O-ethyl-N-ethylpyrrolidinonium triflate (EPEy-TfO), and O-ethyl-N-methylpyrrolidinonium triflate (EMPy-TfO) were previously synthesized by the reaction of amide with alkyl triflate. In addition, NTf₂-based ionic liquids including O-methyl-diethylacetamidium bis(trifluoromethylsulfonyl)imide (MDEA-NTf₂), O-methyl-dimethylformamidium bis(trifluoromethylsulfonyl)imide (MDMF-NTf₂), O-ethyl-dimethylformamidium bis(trifluoromethylsulfonyl)imide (EDMF-NTf₂), and O-ethyl-N-ethylpyrrolidinonium bis(trifluoromethylsulfonyl)imide (EPEy-NTf₂) were previously prepared by anion exchange.²² Moreover, two 1-ethyl-3-methylimidazolium- ([EMIM]-) based ILs, namely, EMIM-TfO and EMIM-NTf₂, were synthesized. Analytical-grade solvents having different Hildebrand solubility parameters, including 2-butanol (22.2 MPa^{1/2}), dimethylacetamide (22.7 MPa^{1/2}), 1-butanol (23.1 MPa^{1/2}), 2-propanol (23.5 MPa^{1/2}), 1-propanol (24.5 MPa^{1/2}), dimethylformamide (24.8 MPa^{1/2}), nitromethane (25.1 MPa^{1/2}), allyl alcohol (25.7 MPa^{1/2}), ethanol (26.5 MPa^{1/2}), dimethyl sulfoxide (26.7 MPa^{1/2}), propylene carbonate (27.3 MPa^{1/2}), 2-pyrrolidone (28.4 MPa^{1/2}), methanol (29.6 MPa^{1/2}), diethylene glycol (29.9 MPa^{1/2}), and ethanolamine (31.3 MPa^{1/2}), were acquired from Sigma-Aldrich.

2.2. Determination of Intrinsic Viscosity. The Hildebrand solubility parameters of ionic liquids at different dissolution temperatures (25, 40, and 60 °C) were determined by measuring their intrinsic viscosities using an Ubbelohde viscometer. Solutions of ionic liquids in different solvents were prepared at five concentrations varying from 0.5% to 5% (v/v). The viscosities of solutions were measured by controlling the temperature. The efflux times were measured at least five times (with the variation of the efflux times being within 0.1 s). The intrinsic viscosity (η , dL/g) was determined from the common intercept of the Huggins and Kraemer relationships, given by

$$\frac{\eta_{sp}}{C} = \eta + k_H \eta^2 C \quad (2)$$

$$\frac{\ln \eta_t}{C} = \eta + k_k \eta^2 C \quad (3)$$

by fitting of the specific viscosity [$\eta_{sp} = (t_{solution} - t_{solvent})/t_{solvent}$] per unit concentration and the natural logarithm of the

relative viscosity ($\eta_r = t_{solution}/t_{solvent}$) per unit concentration versus concentration (C , g/dL). k_H and k_k are the Huggins and Kraemer constants, respectively, and $t_{solution}$ and $t_{solvent}$ are the efflux times of solution and solvent, respectively.

2.3. Determination of Hildebrand Solubility Parameter. To determine the Hildebrand solubility parameters of ionic liquids, the intrinsic viscosities versus the Hildebrand solubility parameters of different solvents were plotted and fitted by the Mangaraj equation

$$\eta = \eta_{max} \exp[-A(\delta_{solvent} - \delta_{IL})^2] \quad (4)$$

where η_{max} is the maximum intrinsic viscosity; A is a constant; and $\delta_{solvent}$ and δ_{IL} are the Hildebrand solubility parameters of the solvent and the ionic liquid, respectively. δ_{IL} , A , and η_{max} were obtained from curve fitting with the OriginPro 8 program.

2.4. Determination of Density. The densities of the ionic liquids were determined at different temperatures using an Anton Paar DMA 35 version 3 portable density meter. Prior to each property measurement, the ionic liquids were vacuum-dried for 20 h at 70 °C and 10⁻³ mbar. Estimates of errors reported in tables and in figures are within 5%.

3. RESULTS AND DISCUSSION

3.1. Influence of Cation and Anion. The Hildebrand solubility parameters of TfO-based and NTf₂-based ionic liquids were determined at 25 °C to investigate the influence of ionic-liquid type. Figure 1a shows the effects of the cation and anion on the Hildebrand solubility parameters of the

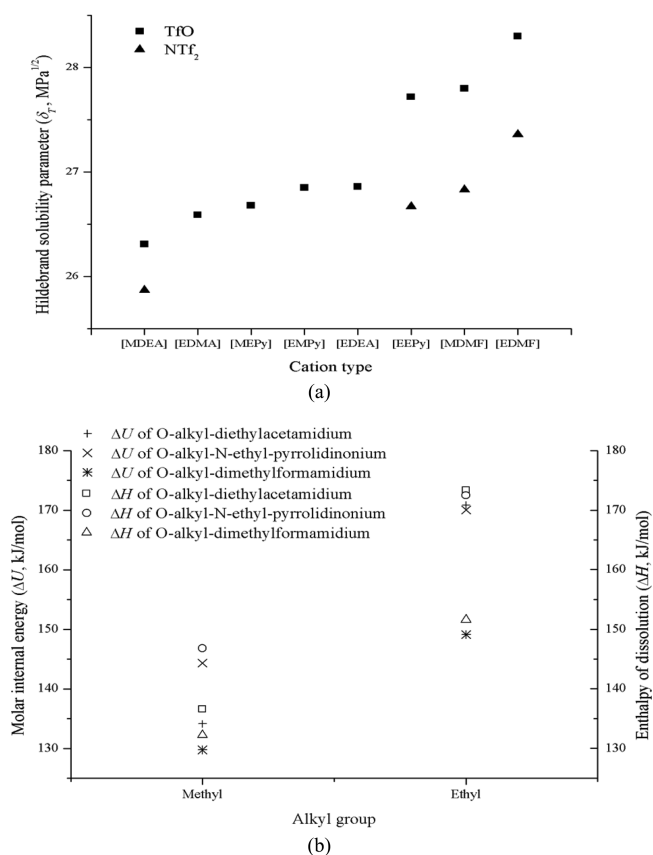
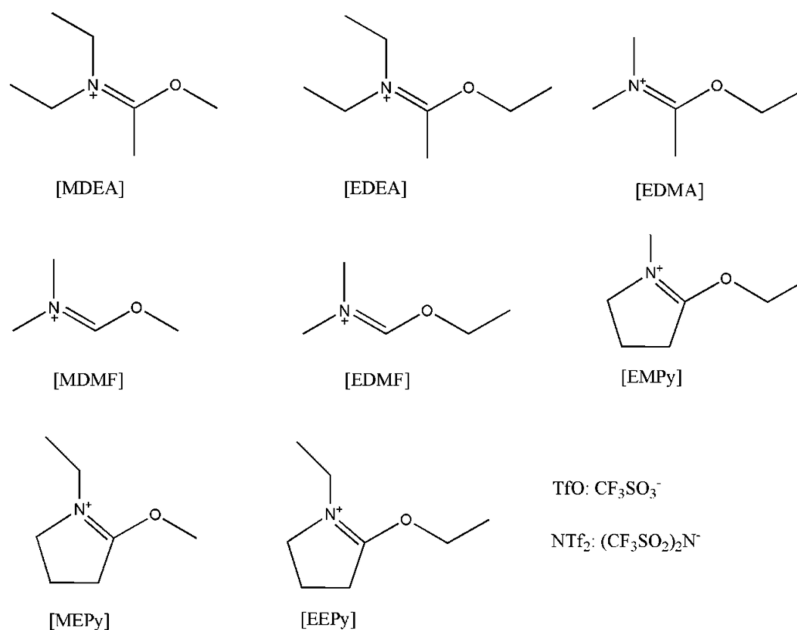


Figure 1. Effects of anion and cation type on (a) Hildebrand solubility parameter and (b) molar internal energy and enthalpy of dissolution measured at 25 °C.

Scheme 1. Structures and Abbreviations of Cations and Anions Studied in This Work



investigated ionic liquids. For the series of TfO-based ionic liquids, EDMF-TfO presents the highest Hildebrand solubility parameter ($\delta_T = 28.30$), whereas MDEA-TfO gives the lowest value ($\delta_T = 26.31$). The values of ionic liquids containing the TfO anion are in the following order: [EDMF] > [MDMF] > [EEPy] > [EDEA] > [EMPy] > [MEPy] > [EDMA] > [MDEA]. It was observed that substitution of the ethyl group on the nitrogen atom of TfO-based ionic liquids tends to increase the Hildebrand solubility parameter, as demonstrated in the cases of EEPy-TfO > EMPy-TfO and EDEA-TfO > EDMA-TfO. For the *O*-alkyl diethylacetamidium, *O*-alkyl-*N*-ethylpyrrolidinium, and *O*-alkyl dimethylformamidium families of TfO-based ionic liquids, the Hildebrand solubility parameters of the *O*-ethyl ionic liquids are greater than those of the *O*-methyl ionic liquids, with EDEA-TfO > MDEA-TfO, EEPy-TfO > MEPy-TfO, and EDMF-TfO > MDMF-TfO.

In addition, it was found that two pairs of TfO-based ionic liquids exhibit similar Hildebrand solubility parameters, namely, EMPy-TfO ($\delta_T = 26.85$) and EDEA-TfO ($\delta_T = 26.86$), as well as EMPy-TfO ($\delta_T = 26.85$) and MEPy-TfO ($\delta_T = 26.68$). For the ionic-liquid pair EMPy-TfO and EDEA-TfO, there is no similarity in the structures of the [EMPy] and [EDEA] cations except for the common *O*-terminal ethyl tail (Scheme 1). Likewise, although the cations of the ionic-liquid pair EMPy-TfO and MEPy-TfO, being pyrrolidinium-based, have the same molecular weight, their ether moieties differ structurally, with the former having an *O*-terminal rodlike CH_2CH_3 tail and the latter having a spherical CH_3 tail. According to the three-dimensional solubility-parameter system proposed by Hansen, the cohesive energy density arises from atomic dispersive interactions, molecular permanent dipole–permanent dipole interactions, and molecular hydrogen-bonding interactions. Overall, the Hildebrand solubility parameter can be expressed in terms of partial or Hansen solubility parameters as $\delta_T = (\delta_D^2 + \delta_P^2 + \delta_H^2)^{1/2}$, where δ_D , δ_P and δ_H are the partial solubility parameters of Hansen representing the contributions from dispersion, polar, and hydrogen-bonding interactions, respectively.¹⁰ To comprehend how the TfO-based ionic-liquid pairs can have similar Hildebrand solubility parameters despite the

differences in cation structure, an attempt was made to determine the partial solubility parameters of these ionic-liquid pairs using an extended regression model.²³ To determine the partial solubility parameters of the ionic liquids, the natural logarithms of the intrinsic viscosities of ionic liquids in different solvents were regressed against the Hansen solubility parameters of a series of solvents

$$\ln \eta = C_0 + C_1\delta_{D,i} + C_2\delta_{D,i}^2 + C_3\delta_{P,i} + C_4\delta_{P,i}^2 + C_5\delta_{H,i} + C_6\delta_{H,i}^2 \quad (5)$$

where $\delta_{D,i}$, $\delta_{P,i}$ and $\delta_{H,i}$ are the partial solubility parameters of solvent representing contributions from the dispersion, polar, and hydrogen-bonding interactions, respectively, and C_0 – C_6 are constant coefficients. The coefficients were obtained from multiple regression analysis using the OriginPro 8 program. From the values of the regression coefficients in eq 5, the partial solubility parameters of the ionic-liquid pairs were calculated as

$$\delta_{D,IL} = -\left(\frac{C_1}{2C_2}\right) \quad (6)$$

$$\delta_{P,IL} = -\left(\frac{C_3}{2C_4}\right) \quad (7)$$

$$\delta_{H,IL} = -\left(\frac{C_5}{2C_6}\right) \quad (8)$$

and their total solubility parameters are summarized in Table 1.

Although there are slight deviations between the total solubility parameters obtained experimentally (1D method) and those evaluated from the partial solubility parameters (3D method), the differences in the values obtained by the two methods (0.09–1.03) are consistent with those found in previous work for other ionic-liquid types.²³ This indicates that the 3D method can be applied to attain a more profound description of the molecular interactions of the ionic liquids of interest. From Table 1, it is noted that both EDEA-TfO and

Table 1. Partial and Total Solubility Parameters of Selected Ionic Liquids

solubility parameters (MPa ^{1/2})	EDEA-TfO		EMPy-TfO		MEPy-TfO	
	1D method	3D method	1D method	3D method	1D method	3D method
dispersion solubility parameter, δ_D	–	14.65	–	16.51	–	13.09
polar solubility parameter, δ_P	–	10.07	–	11.86	–	9.51
hydrogen-bonding solubility parameter, δ_H	–	20.01	–	15.93	–	21.34
total or Hildebrand solubility parameter, δ_T	26.86	26.77	26.85	25.82	26.68	26.78

MEPy-TfO exhibit slightly lower dispersion and polar solubility parameters than EMPy-TfO but higher hydrogen-bonding capacities than EMPy-TfO. This shows that, although the two sets of ionic-liquid pairs (1, EDEA-TfO and EMPy-TfO; 2, MEPy-TfO and EMPy-TfO) provide similar total solubility parameters, upon splitting the values into partial solubility parameters, a substantial difference exists in the molecular interactions of the samples.

When considering the effects of the anion on the Hildebrand solubility parameter, the NTf₂-based ionic liquids were found to present lower values than the TfO-based ionic liquids (Figure 1a). The values for ionic liquids containing the NTf₂ anion are presumably in the same order as those for ionic liquids containing the TfO anion, with selected NTf₂-based ionic liquids demonstrating the following order: [EDMF] > [MDMF] > [EETf] > [MDEA]. The Hildebrand solubility parameter is defined in eq 1 as $\delta_T = [(\Delta H - RT)/V]^{1/2}$. Because ionic liquids have negligible vapor pressure, the

enthalpy of dissolution of ionic liquids can be assumed to be equally large. Thus, differences in solubility parameters arise from differences in molar volumes. [NTf₂] has six fluorine atoms, whereas [TfO] has three fluorine atoms. Apparently, repulsive forces between fluorine atoms lead to an increase in the molecular size of the anion. Hence, NTf₂-based ionic liquids with greater fluorination than TfO-based ionic liquids tend to have higher molar volumes and lower solubility parameters for the same cation family.

Table 2 lists the physicochemical properties of both TfO-based and NTf₂-based ionic liquids including density, molar volume, Hildebrand solubility parameter, cohesive energy density, molar internal energy, and enthalpy of dissolution. The molar internal energies and enthalpies of dissolution of TfO-based ionic liquids vary in the ranges of 130.0–170.9 and 132.3–173.3 kJ/mol, respectively, whereas the molar internal energies and enthalpies of dissolution of NTf₂-based ionic liquids vary in the ranges of 145.7–207.8 and 148.2–210.2 kJ/mol, respectively. For the three families of TfO-based ionic liquids *O*-alkyl diethylacetamidium, *O*-alkyl-*N*-ethylpyrrolidinium, and *O*-alkyl dimethylformamidium, the molar internal energies and enthalpies of dissolution of *O*-ethyl ionic liquids are greater than those of *O*-methyl ionic liquids (Figure 1b). This corresponds with the observation that the Hildebrand solubility parameters of *O*-ethyl ionic liquids are higher than those of *O*-methyl ionic liquids. However, it should be noted that the molar internal energies are dependent on both the Hildebrand solubility parameter and the molar volume. The highest Hildebrand solubility parameter ($\delta_T = 28.30$) presented by EDMF-TfO has a lower molar internal energy than EDEA-TfO (149.13 kJ/mol for EDMF-TfO vs 170.86 kJ/mol for EDEA-TfO), which has a lower Hildebrand solubility

Table 2. Solubility Properties of Ionic Liquids at Different Temperatures

chemical	temperature (°C)	density (g/cm ³)	MW (g/mol)	molar volume (cm ³ /mol)	δ_T (MPa ^{1/2})	CED (J/cm ³)	ΔU (kJ/mol)	ΔH (kJ/mol)
Ionic-Liquid Type								
MDEA-TfO	25	1.4413	279.28	193.77	26.31	692.21	134.13	136.61
MDMF-TfO	25	1.4126	237.20	167.92	27.80	772.84	129.77	132.25
MEPy-TfO	25	1.3675	277.26	202.75	26.68	711.82	144.32	146.80
EDEA-TfO	25	1.2385	293.30	236.82	26.86	721.46	170.86	173.33
EDMA-TfO	25	1.3417	265.25	197.70	26.59	707.03	139.78	142.26
EDMF-TfO	25	1.3492	251.22	186.20	28.30	800.89	149.13	151.60
EETf-TfO	25	1.3165	291.29	221.26	27.72	768.40	170.02	172.50
EMPy-TfO	25	1.3123	277.26	211.28	26.85	720.92	152.31	154.79
MDEA-NTf ₂	25	1.4469	410.36	283.61	25.87	669.26	189.81	192.29
MDMF-NTf ₂	25	1.5405	368.28	239.07	26.83	719.85	172.09	174.57
EDMF-NTf ₂	25	1.4946	382.30	255.79	27.36	748.57	191.47	193.95
EETf-NTf ₂	25	1.4460	422.37	292.10	26.67	711.29	207.76	210.24
EMIM-TfO	25	1.3850	260.23	187.89	27.85	775.62	145.73	148.21
EMIM-NTf ₂	25	1.5182	391.31	257.75	26.39	696.43	179.50	181.77
Dissolution Temperature								
MDEA-TfO	25	1.4413	279.28	193.77	26.31	692.22	134.13	136.61
MDEA-TfO	40	1.4132	279.28	197.62	25.83	667.19	131.85	134.46
MDEA-TfO	60	1.3854	279.28	201.59	25.35	642.62	129.54	132.31
MDMF-TfO	25	1.4126	237.20	167.92	27.80	772.84	129.77	132.25
MDMF-TfO	40	1.3639	237.20	173.91	25.95	673.40	117.11	119.72
MDMF-TfO	60	1.3384	237.20	177.23	25.39	644.65	114.25	117.02
MEPy-TfO	25	1.3675	277.26	202.75	26.68	711.82	144.32	146.80
MEPy-TfO	40	1.3468	277.26	205.87	26.41	697.49	143.59	146.19
MEPy-TfO	60	1.3305	277.26	208.39	25.56	653.31	136.14	138.91

parameter ($\delta_T = 26.86$) but a higher molar volume ($186.20 \text{ cm}^3/\text{mol}$ for EDMF-TfO vs $236.82 \text{ cm}^3/\text{mol}$ for EDEA-TfO).

EMIM-TfO and EMIM-NTf₂ are commonly used ionic liquids with Hildebrand solubility parameters of 27.85 and 26.39, respectively. Both imidazolium ionic liquids have been reported to be applied as supported ionic-liquid membranes in carbon dioxide separation from gaseous streams and as solvents in the ligand substitution reactions of Pt(II) complexes, and EMIM-NTf₂ has been used as a solvent in the liquid–liquid extraction of ethanol from its azeotropic mixture with hexane.^{24–26} It is remarkable that the ionic-liquid pairs EMIM-TfO and MDMF-TfO ($\delta_T = 27.80$) and EMIM-NTf₂ and MDEA-TfO ($\delta_T = 26.31$) present similar Hildebrand solubility parameters, considering the differences in their structures. In view of such similarities, MDMF-TfO could be used in place of EMIM-TfO for certain applications because the former is a distillable ionic liquid, affording a recovery of 99 wt % with a purity of up to 97%, which bodes well for the recyclability of ionic liquids. Similarly, MDEA-TfO, demonstrating a distillation recovery of 98 wt % and a purity of up to 89%, could be a substitute for the use of EMIM-NTf₂.²²

3.2. Influence of Temperature. The effects of dissolution temperature on the Hildebrand solubility parameters of O-methylated TfO-based ionic liquids were investigated in this study. The Hildebrand solubility parameters of MDEA-TfO, MDMF-TfO, and MEPy-TfO, in the range of $25.4\text{--}27.8 \text{ MPa}^{1/2}$, decrease with increasing temperature from 25 to 60 °C (Figure 2a). This is consistent with the correlations of the temperature dependence of solubility parameters for liquids, according to which solubility parameter values are expected to decrease with increasing temperature.²⁷ Both MDEA-TfO and MEPy-TfO present almost linear decreases in Hildebrand solubility parameter with increasing temperature from 25 to 60 °C. On the other hand, MDMF-TfO shows a greater decrease in Hildebrand solubility parameter than MDEA-TfO and MEPy-TfO as the temperature increases from 25 to 40 °C, whereas a slight decrease was noted with increasing temperature from 40 to 60 °C. At both 40 and 60 °C, MDEA-TfO and MDMF-TfO exhibit similar Hildebrand solubility parameters with a negligible difference ranging from 0.04 to 0.12 $\text{MPa}^{1/2}$ as compared to a difference of 1.5 $\text{MPa}^{1/2}$ at 25 °C. MDMF-TfO and MDEA-TfO could possibly become better solvents for solutes with lower Hildebrand solubility parameters at increasing temperature.

As mentioned previously, the total solubility parameter can be expressed in terms of partial solubility parameters comprising dispersion, polar, and hydrogen-bonding contributions. Peculiarly, hydrogen-bonding interactions are sensitive to temperature. As temperature rises, there could be a gradual increase in the weakening and breaking of hydrogen bonds, causing the hydrogen-bonding solubility parameters to decrease more rapidly than the others, contributing to the decrease in the total solubility parameter.

Increasing dissolution temperature exerts an effect on the cohesive energy densities of the O-methylated TfO-based ionic liquids (Table 2). As temperature was increased from 25 to 60 °C, cohesive energy densities of MDEA-TfO (in the range of $642.6\text{--}692.2 \text{ J}/\text{cm}^3$), MDMF-TfO (in the range of $644.7\text{--}772.8 \text{ J}/\text{cm}^3$), and MEPy-TfO (in the range of $653.3\text{--}711.8 \text{ J}/\text{cm}^3$) decreased. Figure 2b illustrates the effects of dissolution temperature on the molar internal energy and enthalpy of dissolution. It is observed that MDEA-TfO presents an almost linear decrease in molar internal energy and enthalpy of

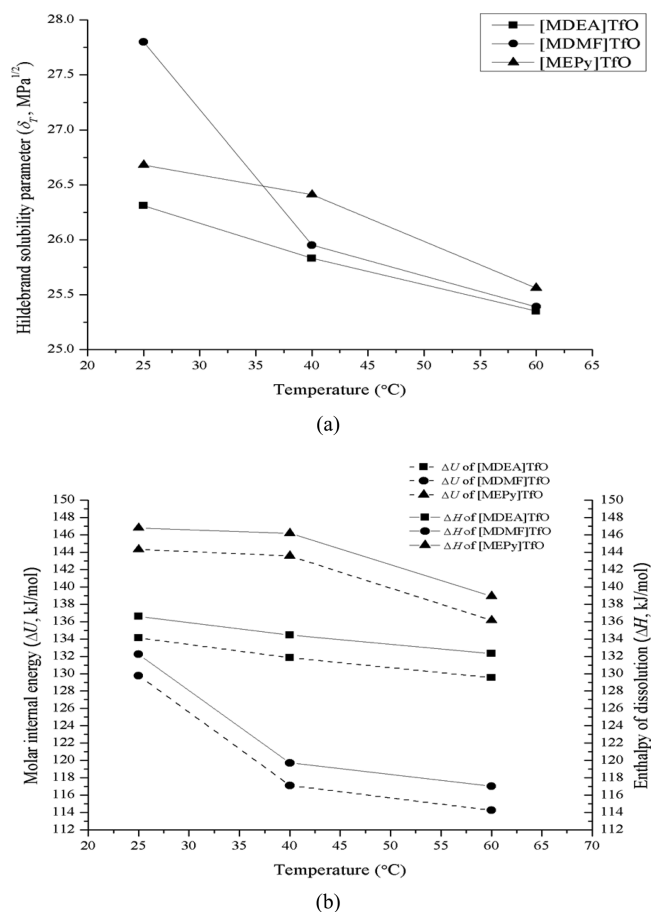


Figure 2. Effects of dissolution temperature on (a) Hildebrand solubility parameter and (b) molar internal energy and enthalpy of dissolution.

dissolution as the temperature is increased from 25 to 60 °C, ranging from 129.5 to 134.1 kJ/mol and from 132.3 to 136.6 kJ/mol , respectively. The molar internal energy and enthalpy of dissolution of MDMF-TfO, in the ranges of 114.3–129.8 and 117.0–132.3 kJ/mol , respectively, decreased as the temperature was increased from 25 to 60 °C. For MEPy-TfO, there was almost no effect on the molar internal energy and enthalpy of dissolution as the temperature was increased from 25 to 40 °C. Rather, an average molar internal energy of 144.0 kJ/mol and an average molar internal energy of 146.5 kJ/mol were observed. On the contrary, as the temperature was increased from 40 to 60 °C, there was a slight decrease in molar internal energy and enthalpy of dissolution, in the ranges of 136.1–143.6 and 138.9–146.2, respectively.

4. CONCLUSIONS

In this study, the Hildebrand solubility parameters of amidium ionic liquids were determined using the intrinsic viscosity approach. The nature of the ion exerts an effect on the Hildebrand solubility parameter, with NTf₂-based ionic liquids presenting lower values than distillable TfO-based ionic liquids. Even though certain ionic liquids belonging to the latter group show similar Hildebrand solubility parameters, their molecular interactions, in particular, hydrogen-bonding interactions, tend to differ, as inferred from the evaluated partial solubility parameters. Moreover, an increase in temperature results in a decrease in the Hildebrand solubility parameters of ionic

liquids. Moreover, both MDMF-TfO and MDEA-TfO were found to have Hildebrand solubility parameters similar to those of the commonly used EMIM-TfO and EMIM-NTf₂, respectively. This is an interesting discovery because it implies that the distillable ionic liquids can potentially be applied in place of the commonly used ionic liquids, addressing the drawback of the high costs and recycling challenges of ionic liquids.

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Notes

The authors declare no competing financial interest.

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