

# The Hildebrand solubility parameters, cohesive energy densities and internal energies of 1-alkyl-3-methylimidazolium-based room temperature ionic liquids

Sang Hyun Lee and Sun Bok Lee\*

Received (in Cambridge, UK) 15th March 2005, Accepted 11th May 2005

First published as an Advance Article on the web 9th June 2005

DOI: 10.1039/b503740a

The Hildebrand solubility parameters, cohesive energy densities and internal energies of 1-alkyl-3-methylimidazolium-based room temperature ionic liquids were determined by the intrinsic viscosity method and their dependencies on the length of the alkyl group analyzed.

Room-temperature ionic liquids (ILs), which are non-volatile, thermally stable and highly polar, are attracting growing interest as alternatives to conventional organic solvents.<sup>1</sup> Recoverability and recyclability also make ILs attractive from industrial and environmental standpoints. When used as solvents in chemical processes, ILs exhibit excellent physical characteristics, including the ability to dissolve polar and non-polar organic, inorganic and polymeric compounds. Moreover, the number of combinations of anions and cations encompassed by ILs is vast, and their associated synthetic flexibility has led to ILs being referred to as 'designer solvents'.<sup>1g</sup> However, in order to be able to realize their potential, one needs to know exactly what is being designed, which parameters are flexible, and which are fixed.<sup>2</sup> It is therefore necessary to understand the link between what is being designed and the fundamental properties that can be measured or predicted. To understand how the physicochemical properties of ILs influence chemical solubility, we first need to understand how the solubility of ILs vary with structure. In this work, we determined the Hildebrand solubility parameters of ILs composed of 1-alkyl-3-methylimidazolium cations and the anions bistrifluoromethanesulfonimide ([Tf<sub>2</sub>N]<sup>-</sup>), hexafluorophosphate ([PF<sub>6</sub>]<sup>-</sup>), and trifluoromethanesulfonate ([TfO]<sup>-</sup>).

The Hildebrand solubility parameter,  $\delta_{\text{H}}$ , is defined as the square root of the cohesive energy density (CED) of a chemical compound:<sup>3</sup>

$$\delta_{\text{H}} = \text{CED}^{1/2} = (\Delta U/V)^{1/2} = [(\Delta H^{\text{vap}} - RT)/V]^{1/2} \quad (1)$$

where  $\Delta U$ ,  $\Delta H^{\text{vap}}$  and  $V$  are the molar internal energy, the enthalpy of vaporization (at 298 K) and the molar volume respectively.  $\delta_{\text{H}}$  has been widely used for predicting the solubilities of various chemicals in organic solvents.<sup>3b</sup> Once  $\delta_{\text{H}}$  and  $V$  values are known, it is possible to estimate  $\Delta U$  and the  $U_2$  parameter, the latter of which has recently been recognized to be an important parameter for determining the solubilities of liquids in water and ILs.<sup>4</sup> Despite its importance, relatively few studies have been conducted to determine the  $\delta_{\text{H}}$  values of ILs.<sup>5</sup>

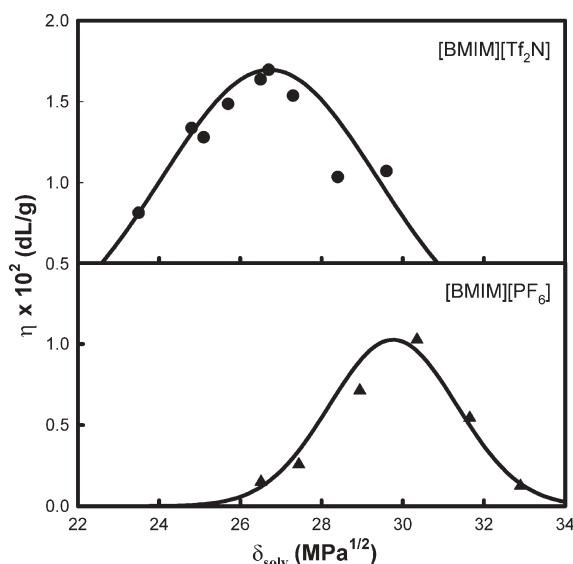
The  $\delta_{\text{H}}$  value of a volatile substance can be conveniently obtained from  $\Delta H^{\text{vap}}$  or vapor pressure-temperature data. However, because of the extremely low vapor pressures of ILs, the direct experimental determination of  $\Delta H^{\text{vap}}$  values is practically impossible, and is the reason why indirect methods are required. Such methods are usually employed for high molecular weight substances including measurements of solubility, osmotic pressure, swelling, and intrinsic viscosity.<sup>3b</sup> Generally most ILs are viscous and their intrinsic viscosities in organic solvents can be easily obtained. Although measurements of solution viscosity have been widely used to estimate the  $\delta_{\text{H}}$  values of polymers,<sup>6</sup> no reports have been issued on the application of this method to ILs. In the present study, we examined whether the  $\delta_{\text{H}}$  of ILs can be estimated by the intrinsic viscosity method.

Viscosity measurements were made at 298 K using an Ubbelohde viscometer. The viscosities in organic solvents were measured for at least 5 solutions containing ILs at levels ranging between 0.2 and 2% (v/v). We selected several ILs based on the combination of the 1-alkyl-3-methylimidazolium cations such as 1-ethyl-3-methylimidazolium ([EMIM]<sup>+</sup>), 1-butyl-3-methylimidazolium ([BMIM]<sup>+</sup>), 1-hexyl-3-methylimidazolium ([HMIM]<sup>+</sup>) and 1-octyl-3-methylimidazolium ([OMIM]<sup>+</sup>), and the anions [Tf<sub>2</sub>N]<sup>-</sup>, [PF<sub>6</sub>]<sup>-</sup> and [TfO]<sup>-</sup>. All ILs used in this study were synthesized and purified by C-TRI (Suwon, Korea) and had a residual chloride content of less than 30 ppm. Efflux times were measured 5 times for each solution after temperature equilibration. Maximum variation in efflux times were less than 0.2%. Intrinsic viscosities,  $\eta$ , were determined by fitting the efflux time-concentration plot with a quadratic equation and extrapolating two common types of viscosity-concentration plots, namely  $\eta_{\text{sp}}/c$  and  $\ln \eta_r$  vs.  $c$ , where  $\eta_{\text{sp}}$  is the specific viscosity,  $\eta_r$  the relative viscosity, and  $c$  the concentration. These plots yielded a common intercept at  $c = 0$ . The standard deviations of  $\eta$  values were less than 2% of the estimated values. Usually,  $\eta$  is a maxima when mutual interaction between solute and solvent is maximal, *i.e.*, when the  $\delta_{\text{H}}$  value of the sample matches with that of the solvent. The same principle can be applied to ILs. To determine  $\delta_{\text{H}}$  values showing maximum intrinsic viscosity, the Mangaraj equation<sup>6g</sup> was used:

$$\eta = \eta_{\text{max}} e^{[-A(\delta_{\text{solv}} - \delta_{\text{IL}})^2]} \quad (2)$$

where  $A$ ,  $\delta_{\text{solv}}$  and  $\delta_{\text{IL}}$  are a constant, the  $\delta_{\text{H}}$  of the solvent and the  $\delta_{\text{H}}$  of the ionic liquid respectively. Fig. 1 shows the regression results of [BMIM][Tf<sub>2</sub>N] and [BMIM][PF<sub>6</sub>] fitted to eqn. (2). The solvents used were 2-butanol ( $\delta_{\text{H}} = 22.2$ ), 1-butanol (23.1), 2-propanol (23.5), 1-propanol (24.5), DMF (24.8), nitromethane

\*sblee@postech.ac.kr



**Fig. 1** Plot of intrinsic viscosities of ILs as a function of  $\delta_H$  of organic solvents (● [BMIM][Tf<sub>2</sub>N], ▲ [BMIM][PF<sub>6</sub>]). The  $\delta_H$  of ILs were determined by fitting intrinsic viscosity data to the equation  $\eta = \eta_{\max} e^{-A(\delta_{\text{solv}} - \delta_{\text{IL}})^2}$ , where  $A$ ,  $\delta_{\text{solv}}$  and  $\delta_{\text{IL}}$  are a constant, the  $\delta_H$  of the solvent and the  $\delta_H$  of the ionic liquid respectively (solid curve).z

(25.1), allyl alcohol (25.7), ethanol (26.5), DMSO (26.7), propylene carbonate (27.3), 2-pyrrolidone (28.4), methanol (29.6), diethylene glycol (29.9), ethylene cyanohydrin (31.0), ethanolamine (31.3), and water (47.9 MPa<sup>1/2</sup>). In the case of [BMIM][PF<sub>6</sub>], ethanol–water mixtures (70–100% ethanol, v/v) were used due to the higher  $\delta_H$  value of this IL. Densities of ILs were measured at 25 °C using a precision electronic balance equipped with the density determination kit (A&D, Japan).

To confirm the reliability of the intrinsic viscosity method, we determined the  $\delta_H$  values of dipropylene glycol (60 cp) and 1,3-butanediol (96 cp), which have viscosities similar to [BMIM][Tf<sub>2</sub>N] (53 cp) and [OMIM][Tf<sub>2</sub>N] (93 cp).<sup>1h</sup> The measured  $\delta_H$  values of dipropylene glycol (26.1 ± 0.3 MPa<sup>1/2</sup>) and 1,3-butanediol (29.0 ± 0.3 MPa<sup>1/2</sup>) were similar to those reported in the literature (26.4 MPa<sup>1/2</sup> and 28.9 MPa<sup>1/2</sup> respectively)<sup>3c</sup> within error ranges, indicating that the intrinsic viscosity method is accurate and comparable to conventional methods. Based on this observation, we extended the viscosity method to determine the solubility parameters of ILs.

The  $\delta_H$ , CED,  $\Delta U$  and  $U_2$  values of the ILs examined in this study are summarized in Table 1. Densities, molecular weights,

and molar volumes are also shown there. CED and  $\Delta U$  were estimated using eqn. (1), and  $U_2$  was obtained by dividing  $\Delta U$  (kJ mol<sup>-1</sup>) by 41.87, as described previously.<sup>4a</sup> Table 1 also shows the  $\delta_H$  values of the ILs reported by Swiderski *et al.*,<sup>5a</sup> who determined solubility parameters from the solvent dependence on the bimolecular rate constant of Diels–Alder reactions. The  $\delta_H$  values reported by Swiderski *et al.*<sup>5a</sup> are in good agreement with those determined by the intrinsic viscosity method. Differences between the  $\delta_H$  values obtained using the two methods were -1.2, +0.4, and -0.5 MPa<sup>1/2</sup> for [BMIM][Tf<sub>2</sub>N], [BMIM][PF<sub>6</sub>] and [BMIM][TfO] respectively, which is within the error ranges reported by Swiderski *et al.*<sup>5a</sup> The error ranges of Swiderski's method (±1.5 MPa<sup>1/2</sup>) are much larger than those of ours (≤ ±0.5 MPa<sup>1/2</sup>). However, considering the difference between the two principles, it is remarkable that they produced such similar values. Our result obtained for [BMIM][PF<sub>6</sub>] (29.8 MPa<sup>1/2</sup>) is also comparable with that predicted by Morrow and Maginn,<sup>5b</sup> who used a computationally-based technique (28.5 MPa<sup>1/2</sup>).

Previous workers usually studied the physicochemical properties of ILs with a variety of anions but the same cation. Accordingly, no systematic study has been undertaken on the effects of cations on the  $\delta_H$ -related parameters of ILs. The results shown in Table 1 indicate that the  $\delta_H$  values of the ILs we studied are influenced by the nature of the anion. However,  $\delta_H$  values are also dependent on the number of carbon atoms in the alkyl chain of the 1-alkyl-3-methylimidazolium cation, ranging from C<sub>2</sub> ([EMIM]<sup>+</sup>) to C<sub>8</sub> ([OMIM]<sup>+</sup>). Moreover, it has been reported that there is no simple relationship between  $\delta_H$  values and alkyl chain length for 1-alkyl derivatives; *i.e.*  $\delta_H$  increases with chain length for homologous series of *n*-alkanes, branched alkanes and alkenes, but decreases for alcohols, ethers, ketones and alkylamines.<sup>7</sup>

In the cases of the ILs examined in this study,  $\delta_H$  and CED values tended to decrease as chain length increased (Table 1). To further examine the dependence of the  $\delta_H$ -related parameters ( $Y$ :  $\delta_H$ , CED,  $\Delta U$  and  $U_2$ ) on the number of carbons,  $N$ , in the alkyl chains of the ILs, they were each plotted against  $N$ . It was found that  $\delta_H$  and associated properties were linearly related to  $N$ . The gradients  $a$ , intercepts  $b$ , and correlation coefficients  $R^2$  of the ILs studied in this work are shown in Table 2. An analysis of these relations indicated that the gradients (changes in a parameter per CH<sub>2</sub> increment) varied little with anion type. For example,  $\delta_H$  values per CH<sub>2</sub> group were -0.42 and -0.50 MPa<sup>1/2</sup> for [Tf<sub>2</sub>N]<sup>-</sup> and [PF<sub>6</sub>]<sup>-</sup> respectively. However, the intercepts differed appreciably; the  $b$  values in Table 2 indicating that the  $\delta_H$  and CED of [PF<sub>6</sub>]<sup>-</sup> were always greater than those of [Tf<sub>2</sub>N]<sup>-</sup> by *ca.* 3.5 MPa<sup>1/2</sup>

**Table 1** Solubility parameters, cohesive energy densities and the internal energies of ILs at 298 K

IL	Density/g cm <sup>-3</sup>	MW/g mol <sup>-1</sup>	Molar volume/cm <sup>3</sup> mol <sup>-1</sup>	$\delta_H$ /MPa <sup>1/2</sup>		CED/J cm <sup>-3</sup>	$\Delta U$ /kJ mol <sup>-1</sup>	$U_2$
				This work <sup>a</sup>	Ref. 5a			
[EMIM][Tf <sub>2</sub> N]	1.519	391.3	257.6	27.6 ± 0.3		761.8	196.2	4.69
[BMIM][Tf <sub>2</sub> N]	1.436	419.4	292.0	26.7 ± 0.3	25.5	712.9	208.2	4.97
[HMIM][Tf <sub>2</sub> N]	1.373	447.4	325.9	25.6 ± 0.3		655.4	213.6	5.10
[OMIM][Tf <sub>2</sub> N]	1.317	475.5	361.0	25.0 ± 0.5		625.0	225.6	5.39
[BMIM][PF <sub>6</sub> ]	1.369	284.2	207.6	29.8 ± 0.3	30.2	888.0	184.3	4.40
[HMIM][PF <sub>6</sub> ]	1.302	312.2	239.8	28.6 ± 0.4		818.0	196.2	4.69
[OMIM][PF <sub>6</sub> ]	1.233	340.3	276.0	27.8 ± 0.2		772.8	213.3	5.09
[BMIM][TfO]	1.296	299.3	230.9	25.4 ± 0.4	24.9	645.2	149.0	3.56

<sup>a</sup> 95% confidence interval (mean ± 2 standard errors) of  $\delta_H$  values obtained by fitting experimental data to eqn. (2).

**Table 2** Constants in the relationship  $Y = aN + b$  for the ILs examined in this study

$Y$	ILs	$a$	$b$	$R^2$
$\delta_{\text{H}}/\text{MPa}^{1/2}$	$[\text{Tf}_2\text{N}]^-$	-0.42	28.3	0.988
	$[\text{PF}_6]^-$	-0.50	31.7	0.987
$\text{CED}/\text{J cm}^{-3}$	$[\text{Tf}_2\text{N}]^-$	-21.7	795	0.987
	$[\text{PF}_6]^-$	-28.8	999	0.985
$\Delta U/\text{kJ mol}^{-1}$	$[\text{Tf}_2\text{N}]^-$	5.1	185	0.972
	$[\text{PF}_6]^-$	7.2	155	0.989
$U_2$	$[\text{Tf}_2\text{N}]^-$	0.12	4.41	0.972
	$[\text{PF}_6]^-$	0.17	3.69	0.989

and *ca.* 200 J cm<sup>-3</sup> respectively, when compared with identical alkyl chain lengths.

Unlike  $\delta_{\text{H}}$  and CED, the values of  $\Delta U$  and  $U_2$  increased with  $N$  because  $V$  increases with  $N$ . Increments of  $\Delta U$  per CH<sub>2</sub> group were estimated to be 5.1 and 7.2 kJ mol<sup>-1</sup> for  $[\text{Tf}_2\text{N}]^-$  and  $[\text{PF}_6]^-$  respectively. It is well known that for homologous series of molecules  $\Delta H^{\text{vap}}$ , and hence  $\Delta U$ , are linearly dependent on alkyl chain length.<sup>8</sup> Recent analyses of *n*-alkanes, 1-alcohols, and 1-alkylamines showed that at 298 K the CH<sub>2</sub> group contributes 4.95 kJ mol<sup>-1</sup> to  $\Delta H^{\text{vap}}$  for compounds that are liquids and *ca.* 8.9 kJ mol<sup>-1</sup> for solids.<sup>8a</sup> Thus, the CH<sub>2</sub> group contribution of ILs, corresponding to 5.1–7.2 kJ mol<sup>-1</sup>, is higher than that of conventional liquid solvents. We postulate that the high enthalpy of CH<sub>2</sub> groups in ILs may be due to electrostatic cation–anion attractions.

In summary, the results of the present study show that the  $\delta_{\text{H}}$  of ILs can be determined by measuring their solution viscosities in a series of solvents with known but varied solubility parameters. We also found that  $\delta_{\text{H}}$ , CED,  $\Delta U$  and  $U_2$  values vary linearly with  $N$  and that the contribution made by the CH<sub>2</sub> group to the  $\Delta U$  of ILs is unusually high compared to conventional liquid solvents. The results obtained provide a means of estimating the  $\delta_{\text{H}}$ -related properties of ILs, and provide useful information for the designing of ILs with specific solubility properties.

**Sang Hyun Lee and Sun Bok Lee\***

Department of Chemical Engineering and Division of Molecular and Life Sciences, Pohang University of Science and Technology, San 31, Hyoja-Dong, Pohang, 790-784, Korea. E-mail: sblee@postech.ac.kr

## Notes and references

- (a) P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH/Verlag, Weinheim, 2003; (b) J. L. Kaar, A. M. Jesionowski, J. A. Berberich, R. Moulton and A. J. Russell, *J. Am. Chem. Soc.*, 2003, **125**, 4125; (c) J. F. Brennecke and E. J. Maginn, *AIChE J.*, 2001, **47**, 2384; (d) R. Sheldon, *Chem. Commun.*, 2001, 2399; (e) M. J. Earle and K. R. Seddon, *Pure Appl. Chem.*, 2000, **72**, 1391; (f) T. Welton, *Chem. Rev.*, 1999, **99**, 2071; (g) M. Freemantle, *Chem. Eng. News*, 1998, **76**, 32; (h) C. F. Poole, *J. Chromatogr., A*, 2004, **1037**, 49.
- L. Crowhurst, P. R. Mawdsley, J. M. Perez-Arlandis, P. A. Salter and T. Welton, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2790.
- (a) J. H. Hildebrand and R. L. Scott, *The Solubility of Non-Electrolytes*, Prentice-Hall, New York, 3rd edn., 1950; (b) A. F. M. Barton, *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Boca Raton, FL, 2nd edn., 1991; (c) C. M. Hansen, *Hansen Solubility Parameters: A User's Handbook*, CRC Press, Boca Raton, FL, 1999, pp. 167–195.
- (a) S. B. Lee, *J. Chem. Technol. Biotechnol.*, 2005, **89**, 133; (b) S. B. Lee, *J. Pharm. Sci.*, 1996, **85**, 348; (c) S. B. Lee, *J. Ferment. Bioeng.*, 1995, **80**, 141.
- (a) K. Swiderski, A. McLean, C. M. Gordon and D. H. Vaughan, *Chem. Commun.*, 2004, **19**, 2178; (b) T. I. Morrow and E. J. Maginn, *J. Phys. Chem. B*, 2002, **106**, 12807.
- (a) P. Bustamante, J. Navarro-Lupion and B. Escalera, *Eur. J. Pharm. Sci.*, 2005, **24**, 229; (b) J. K. Jeong and D. C. Lee, *Korea Polym. J.*, 1996, **4**, 9; (c) U. Siemann, *Eur. Polym. J.*, 1992, **28**, 293; (d) R. Mieczkowski, *Eur. Polym. J.*, 1991, **27**, 377; (e) C. Marco, A. Bello, J. G. Fatou and J. Garza, *Makromol. Chem.*, 1986, **187**, 177; (f) M. B. Huglin and D. J. Pass, *J. Appl. Polym. Sci.*, 1968, **12**, 473; (g) D. Mangaraj, S. K. Bhatnager and S. B. Rath, *Makromol. Chem.*, 1963, **67**, 75.
- (a) A. E. Rheineck and K. F. Lin, *J. Paint Technol.*, 1968, **40**, 611; (b) A. H. Konstam and W. R. Fearheller, Jr., *AIChE J.*, 1970, **16**, 837.
- (a) D. Matulis, *Biophys. Chem.*, 2001, **93**, 67; (b) J. S. Chickos and W. Hanshaw, *J. Chem. Eng. Data*, 2004, **49**, 620.