

Solubility Parameters based on Refractive Index Data of Ionic Liquid

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ABSTRACT

This article reports on the estimation of solubility parameters using refractive index for a series of imidazolium-based ionic liquids (ILs) and their dependencies on the carbon number of alkyl side-chain of cation and anion. Gathering about 35 ILs of refractive indices data from the literature, the solubility parameters estimation fit well with the suggested correlation. The precision of the estimated solubility parameters obtained indicates that the refractive index-solubility parameters correlation can be an alternative tool to estimate solubility parameter value for ILs.

INTRODUCTION

Ionic liquids (ILs) are usually being referred as “designer solvent” due to their associated synthetic flexibility with vast number of combinations of cation and anion [1-3]. With the numbers of combinations keep increasing, the need to understand the properties is important for their potential and also for the researchers to modify the structure to cater for specific industrial applications. One of the importance properties is solubility parameter, δ .

Solubility parameter, δ , is an important predictive tool for solubility study, especially for solubilities between polymers and solvents [4]. It is widely used for correlating polymers and solvents interaction. Generally, δ is an estimated value which is highly desirable in order to study the substance characteristics particularly in diffusions, solubilities and transport phenomena [5-6]. For the ILs series, the existing methods reported in the literatures for estimating the solubility parameters are not straight forward calculation which opportunely obtained inconsistent values. Therefore, in this work another approach which is convenient for a quick estimation of the solubility parameter for the ILs is proposed. This article reports on the estimation of the solubility parameters values for 35 of ILs using refractive index as a base of calculation, where the data were collected from the literatures. The approach has been applied on the polymers as reported in Lawson & Ingham (1969) [6], and the same concept has been applied for the selected ILs.

THEORY

Firstly, the approach has been taken into account by relying on the Coulombic nature similarity of associated solution by polymers and anion-cation complexity of interactions in ILs. The works presented here was largely referred to imidazolium-based ILs and the theory is originally based on solubility parameters estimation for polymers [6]. All refractive index data of ILs was taken from previous published literatures [7-22]. It should be acknowledgeable that, further work would be required in order to determine the solubility parameter for others type based-ILs if possible.

Accordingly stated by Fedors (1974) [4], Lawson and Ingham (1969) [6] and Wingefors (1981) [23], the solubility parameter is given by,

$$\delta^2 = \frac{\Delta H_v - RT}{V} \quad (1)$$

where ΔH_v , R , T and V is heat of vaporization per mole, molar gas constant, absolute temperature unit and molar volume unit, respectively. Unfortunately with ILs frequent exhibit as non-volatile liquids [5], the above equation cannot be employed. Then, Lawson and Ingham (1969) [6] utilized and simplified the relationship between heat of vaporization and refractive index from latent heat of vaporization that previously derived by Walden in 1910 [6];

$$\Delta H_v \cong C \left(\frac{n^2 - 1}{n^2 + 2} V \right) \quad (2)$$

where C and n are constant and refractive index, respectively. Then, by substituting Equation 2 into Equation 1, the relationship between refractive index and solubility parameter can be attained as shown in Equation 3.

$$\delta \cong \sqrt{\left[C \left(\frac{n^2 - 1}{n^2 + 2} \right) - \frac{RT}{V} \right]} \quad (3)$$

Using the above relationship, a simple correlation of the refractive index and the solubility parameter (in cal.cm^{-3}) can be obtained using least square curve fit of the solubility parameter, δ and the Lorentz-Lorenz function. By utilizing refractive index into the equation expression which then initially opens the view by introducing the relationship for ILs. As suggested by Lawson and Ingham (1969) [6], the RT term can be dropped due to the very small values as compared to ΔH_v term and ideally to give a straight line fit passed through the origin. The solubility parameter value obtained was then converted to standard unit (in $\text{MPa}^{1/2}$) for evaluation and comparison purposes.

RESULT & DISCUSSION

Figure 1 shows the regression results of the estimated solubility parameters, δ , as a function of Lorentz-Lorenz for 35 ILs, by applying Equation 3 at 298.15 K. The straight line fit is obtained which pass through the origin with a slope constant, A of 17.607, in agreement with Lawson and Ingham (1969) [6] suggestion.

The estimated δ values are shown in Table 1 for 35 studied ILs. An analysis indicates that the increasingly changes in δ values per C_nH_{n+2} ($n = 2, 4, 6, 8, 10, 12$) increment with certain anion type.

For example, as being depicted in the Figure 2, $[NTf_2]$ and $[PF_6]$ anion showed an increment in δ values as the number of carbons in the alkyl side-chain of the imidazolium-based cation increased. $[BF_4]$ and $[OTf]$ anions also showed an increment in δ values.

On the other hand, as for the 35 ILs studied here, $[MSO_4]$, $[OSO_4]$, $[ESO_4(ME)]$, $[Cl]$ anion showed a decrease in the values with an increase of the alkyl side-chain. In other words, the more aliphatic the cation is, the higher the solubility parameter for $[NTf_2]$, $[PF_6]$, $[BF_4]$ and $[OTf]$ anions, but lower for $[MSO_4]$, $[OSO_4]$, $[ESO_4(ME)]$, $[Cl]$ anions and vice versa.

Figure 3 (a-d) shows the influence of anion on the δ values for imidazolium-based ILs. For alkyl side-chain (from $C_2 - C_8$), the δ values increases in the following order: $[NTf_2] < [OTf] < [OSO_4] < [ESO_4] < [TOS]$; $[PF_6] < [BF_4] < [NTf_2] < [OTf] < [OSO_4] < [ClO_4] < [MSO_4] < [ESO_4(ME)] < [OAc] < [Br] < [I]$; $[PF_6] < [BF_4] < [NTf_2] < [Cl]$; $[PF_6] < [BF_4] < [NTf_2] < [ESO_4(ME)] < [Cl]$ for ethyl, butyl, hexyl and octyl substitutes, respectively. By considering only on anion type which subsequently due to the similar cation, $[PF_6]$ showed the lowest in δ values for imidazolium-based ILs while $[Cl]$ showed the highest one. One possible explanation is that, the refractive index of $[Cl]$ is higher as compared to $[PF_6]$ anion. It can be deduced that, the higher the refractive index, the higher would be the solubility parameters. In general, when the compound is denser or, in other words, the molecules are tightly packed, the refractive index of that substance is expected to be high [7].

The δ values presented here are indirectly followed the trend as obtained by previous studies as tabulated in Table 2. As in the previous studies Lee and Lee (2005) [1]; Marciniak (2010) [2]; Mutelet *et al.* (2005) [3]; Camper *et al.* (2005) [24] and Swiderski *et al.* (2004) [25], it was indicated that δ values decreased as the number of carbons in the alkyl side-chain of the imidazolium-based cation increased. Meanwhile, in intrinsic viscosity method proposed by Lee and Lee (2005) [1], for ILs ranging from C_2mim $[NTf_2]$ to C_8mim $[NTf_2]$, the inconsistently decrement was observed with the increase of number of carbons in the alkyl side-chain. But, the present study showed a coherent increment in δ values as the number of carbon in the alkyl side-chain increased.

From our observations, there are huge value gaps in estimating δ between the previous studied methods including intrinsic viscosity method as such. But, at a very least, the δ values which obtained from intrinsic viscosity method and Kamlet-Taft equation are relatively consistent within the range of ± 1.2 . On the other hand, as computed using modified Kapustinskii equation, the δ obtained are extremely high above 38 while other estimations in dated values below 32. Bara *et al.* (2009) [26] initially stated that solubility parameters calculated from modified Kapustinskii equation, not appeared to be the most appropriate values because this approach originally meant for alkali metal salts which behave differently compared to imidazolium-based ILs.

CONCLUSION

Through this work, initially it can be deduced that δ values can be estimated from refractive index data. The δ values showed an increment with the increased of alkyl side-chain of imidazolium-based cation for [NTf₂], [PF₆], [BF₄] and [OTf] anion but not for [MSO₄], [OSO₄], [ESO₄(ME)] and [Cl] anion which showed a decrement in δ values. Besides that, most of the δ value is tenderly high if that ILs showed high in refractive index values.

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Figures and Tables Legend

Figure 1: Solubility parameter, δ (cal. cm⁻³) vs. LL for 35 ILs at 298.15 K

Figure 2: Solubility parameter, δ (MPa^{1/2}) as a function of the number of carbons in the alkyl side chain of imidazolium-based cation

Figure 3: Anion influence on the solubility parameter, δ (MPa^{1/2}) for ILs based on:
(a) C₂mim; (b) C₄mim; (c) C₆mim; (d) C₈mim

Table 1: Solubility parameters, δ (MPa^{1/2}) estimated from refractive index data of ILs

Table 2: Comparison solubility parameter, δ (MPa^{1/2}) between present work and existing methods

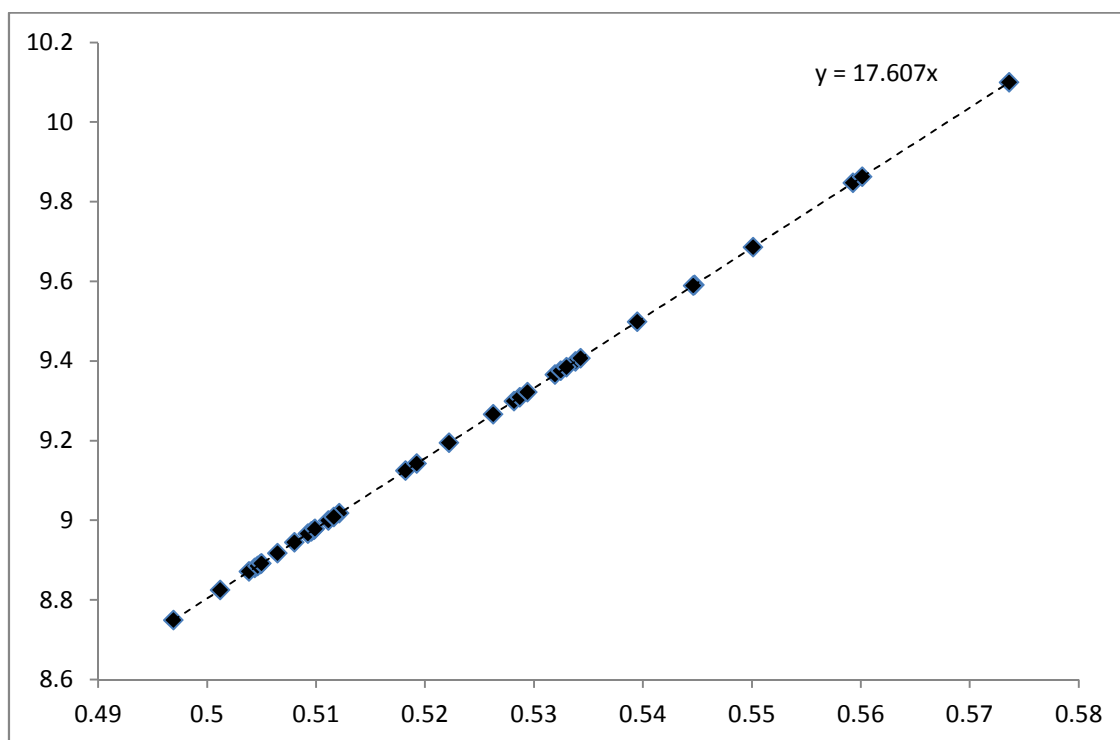
δ (cal.cm⁻³)**Lorentz-Lorenz (LL) function**

Figure 1: Solubility parameter, δ (cal. cm⁻³) vs. LL for 35 ILs at 298.15 K

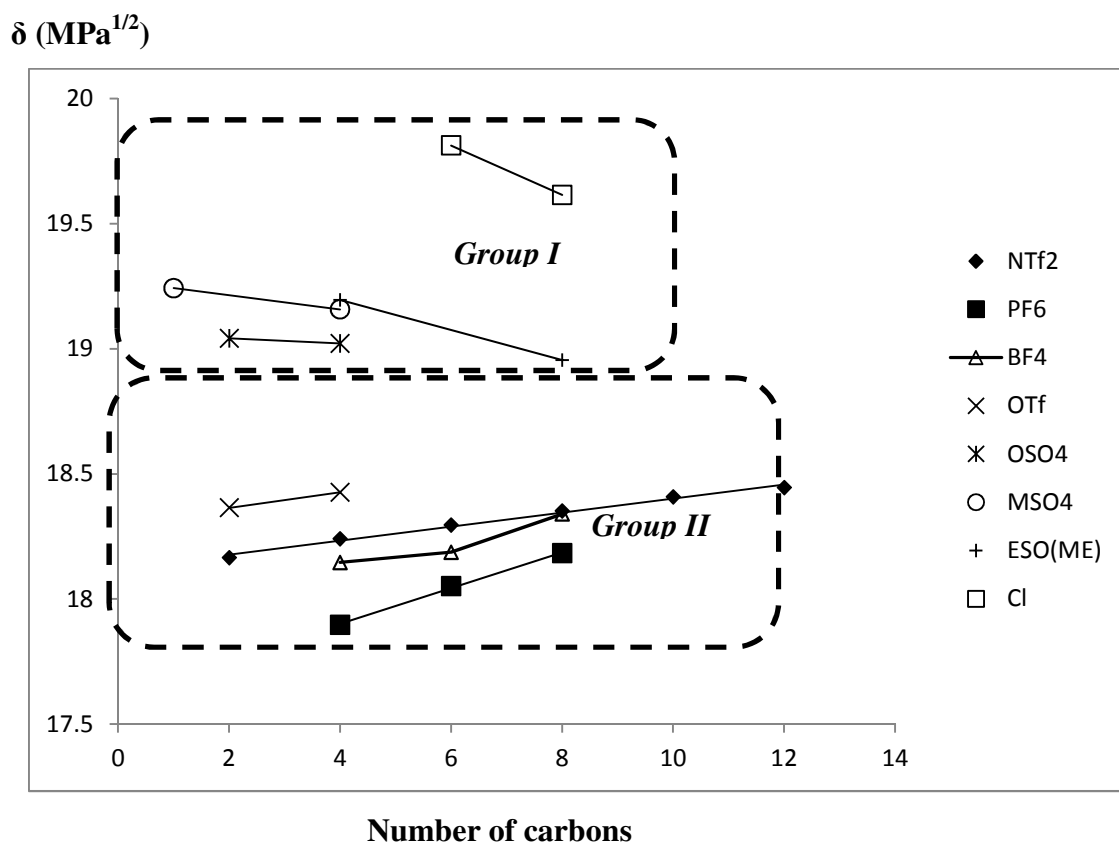
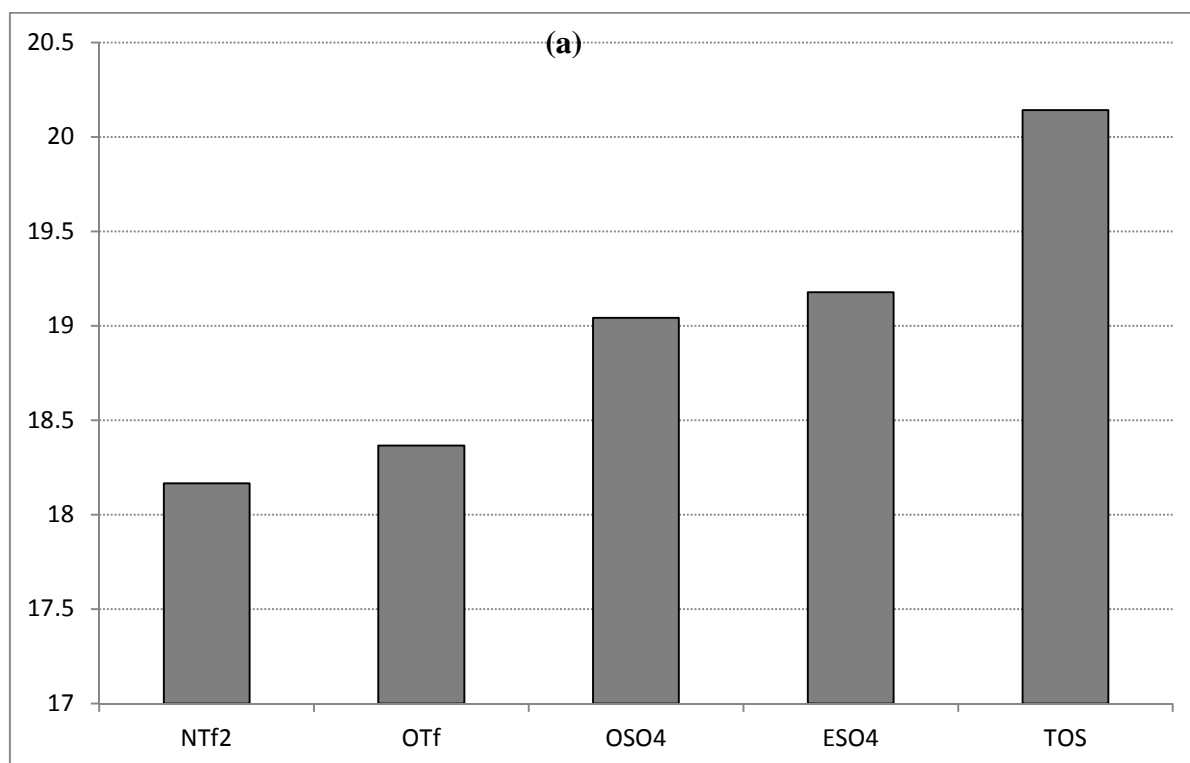
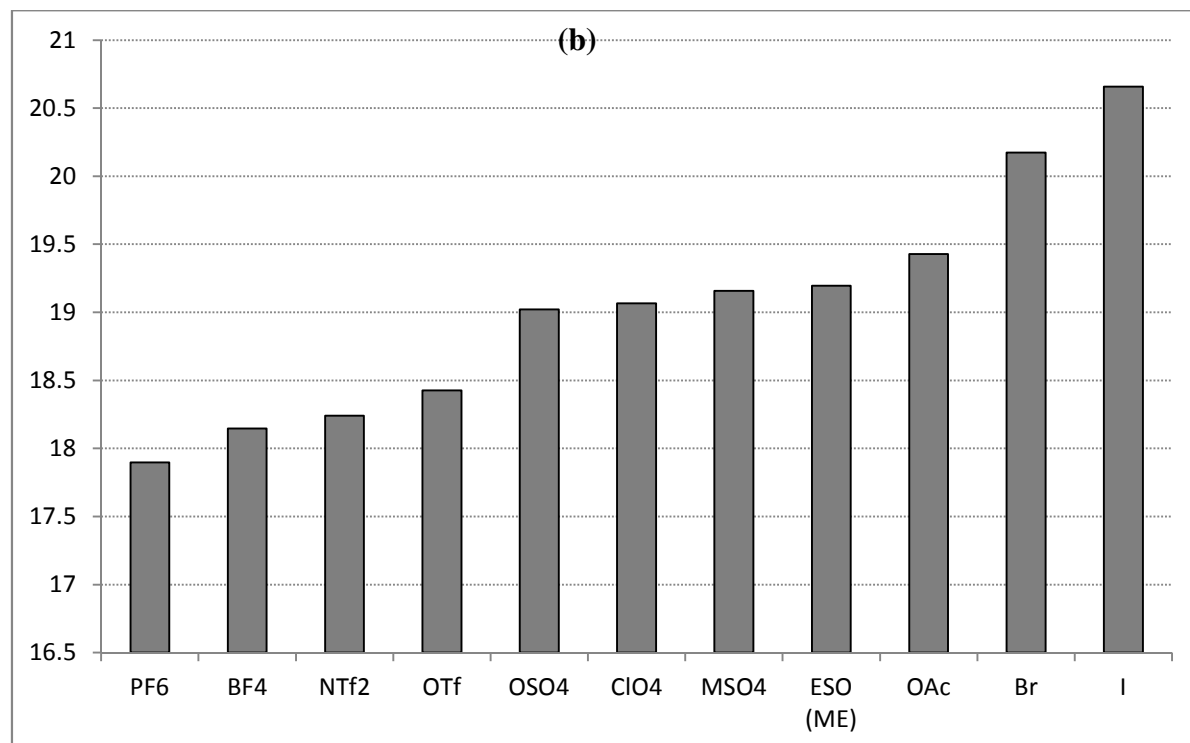


Figure 2: Solubility parameter, δ ($\text{MPa}^{1/2}$) as a function of the number of carbons in the alkyl side chain of imidazolium-based cation

Group I : The solubility parameter, δ decrease with the number of carbons in the alkyl side-chain of imidazolium-based cation

Group II: The solubility parameter, δ increase with the number of carbons in the alkyl side-chain of imidazolium-based cation

δ (MPa^{1/2}) δ (MPa^{1/2})

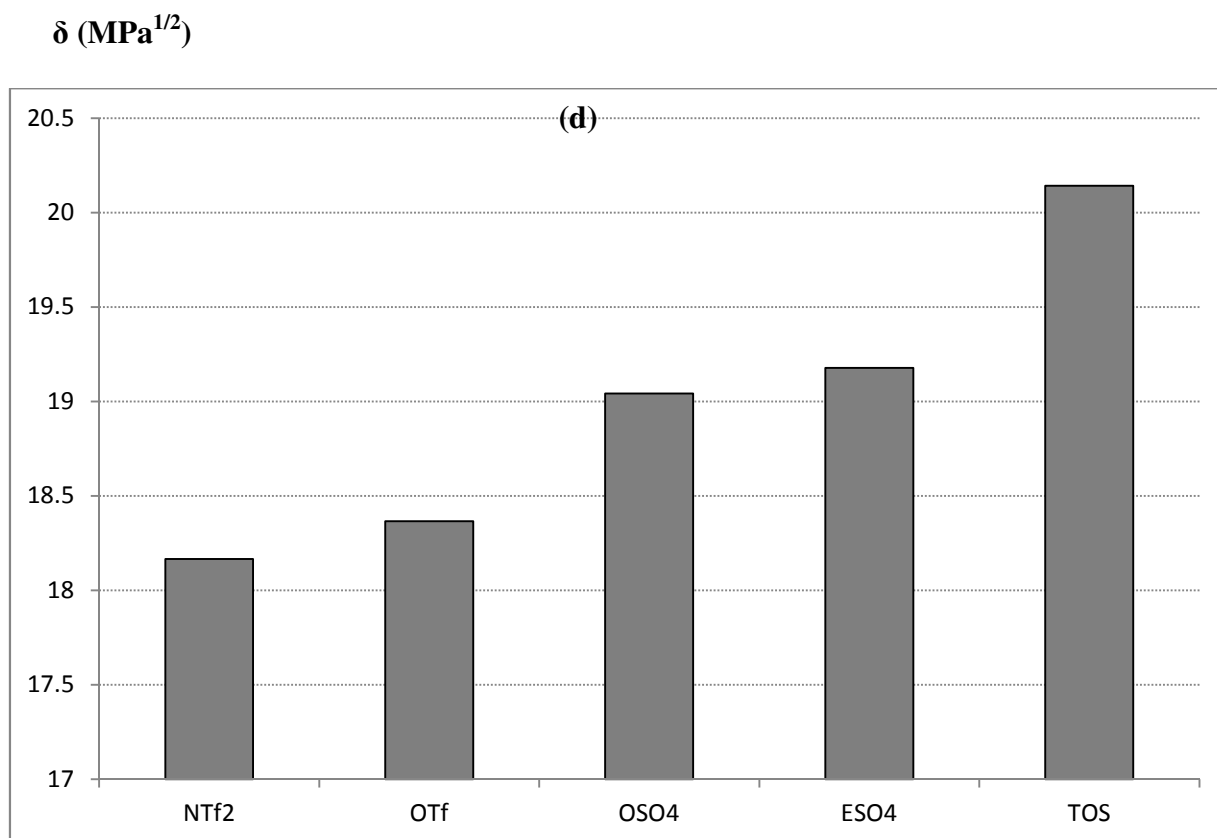
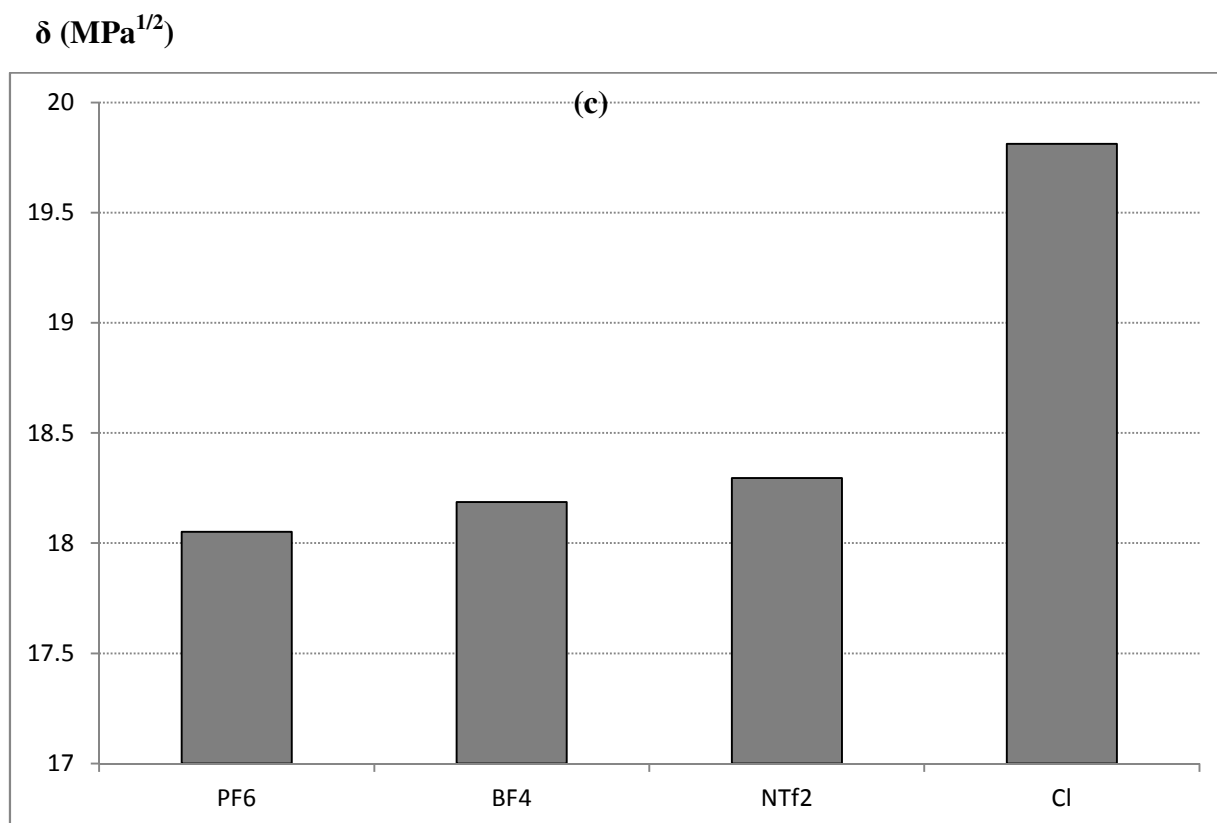


Figure 3: Anion influence on the solubility parameter, δ (MPa^{1/2}) for ILs based on: (a) C₂mim; (b) C₄mim; (c) C₆mim; (d) C₈mim

Table 1: Solubility parameters, δ (MPa^{1/2}) estimated from refractive index data of ILs

| ILs | δ (MPa ^{1/2}) | ILs | δ (MPa ^{1/2}) |
|--|--------------------------------|---|--------------------------------|
| C ₂ mim NTf ₂ | 18.165 | C ₂ mim OTf | 18.364 |
| C ₄ mim NTf ₂ | 18.240 | C ₄ mim OTf | 18.426 |
| C ₆ mim NTf ₂ | 18.296 | P _{6,6,6,14} OTf | 18.807 |
| C ₈ mim NTf ₂ | 18.352 | C ₂ mim OSO ₄ | 19.041 |
| C ₁₀ mim NTf ₂ | 18.408 | C ₄ mim OSO ₄ | 19.021 |
| C ₁₂ mim NTf ₂ | 18.445 | C ₁ mim MSO ₄ | 19.242 |
| C ₄ mpyr NTf ₂ | 18.175 | C ₄ mim MSO ₄ | 19.157 |
| P _{6,6,6,14} NTf ₂ | 18.663 | C ₄ mim OAc | 19.429 |
| C ₄ mim BF ₄ | 18.146 | P _{6,6,6,14} OAc | 19.226 |
| C ₆ mim BF ₄ | 18.187 | C ₂ mim ESO ₄ | 19.177 |
| C ₈ mim BF ₄ | 18.340 | C ₂ py ESO ₄ | 19.618 |
| C ₄ dmim BF ₄ | 18.360 | C ₄ mim(ME) ESO ₄ | 19.195 |
| C ₄ mpy BF ₄ | 18.701 | C ₈ mim(ME) ESO ₄ | 18.954 |
| C ₄ mim PF ₆ | 17.897 | C ₆ mim Cl | 19.812 |
| C ₆ mim PF ₆ | 18.051 | C ₈ mim Cl | 19.614 |
| C ₈ mim PF ₆ | 18.183 | C ₄ mim I | 20.659 |
| C ₄ mim ClO ₄ | 19.067 | C ₄ mim Br | 20.173 |
| C ₂ mim TOS | 20.142 | | |

Table 2: Comparison solubility parameter, δ (MPa^{1/2}) between present work and existing methods

| ILs | This work | Intrinsic viscosity | IGC | Kapustinskii | Kamlet-Taft |
|-------------------------------------|-----------|---------------------|----------------------|----------------------|----------------------|
| C ₂ mim NTf ₂ | 18.165 | 27.6 ^[1] | - | 38.4 ^[24] | - |
| C ₄ mim NTf ₂ | 18.240 | 26.7 ^[1] | - | - | 25.5 ^[25] |
| C ₆ mim NTf ₂ | 18.296 | 25.6 ^[1] | 20.25 ^[2] | - | - |
| C ₈ mim NTf ₂ | 18.352 | 25.0 ^[1] | - | - | - |
| C ₄ mim BF ₄ | 18.146 | 31.6 ^[1] | 24.3 ^[3] | 47.4 ^[24] | - |
| C ₆ mim BF ₄ | 18.187 | - | 23.3 ^[3] | - | - |
| C ₈ mim BF ₄ | 18.340 | - | 22.5 ^[3] | - | - |
| C ₄ mim PF ₆ | 17.897 | 29.8 ^[1] | - | 43.8 ^[24] | 30.2 ^[25] |
| C ₆ mim PF ₆ | 18.051 | 28.6 ^[1] | - | - | - |
| C ₈ mim PF ₆ | 18.183 | 27.8 ^[1] | - | - | - |
| C ₂ mim OTf | 18.364 | - | - | 47.2 ^[24] | - |
| C ₄ mim OTf | 18.426 | 24.9 ^[1] | 22.67 ^[2] | - | 25.4 ^[25] |
| C ₄ mim OSO ₄ | 19.021 | - | 22.83 ^[2] | - | - |
| C ₈ mim Cl | 19.614 | - | 19.91 ^[3] | - | - |

ABBREVIATION

| Anion | |
|------------------------|---|
| NTf ₂ | Bis(trifluoromethylsulfonyl)imide |
| BF ₄ | Tetrafluoroborate |
| PF ₆ | Hexafluorophosphate |
| OTf | Trifluoromethanesulfonate |
| OSO ₄ | Octylsulfate |
| MSO ₄ | Methylsulfate |
| ESO ₄ | Ethylsulfate |
| OAc | Acetate |
| Cl | Chloride |
| Br | Bromide |
| I | Iodide |
| Cation | |
| C ₁ mim | 1,3-dimethylimidazolium |
| C ₂ mim | 1-ethyl-3-methylimidazolium |
| C ₄ mim | 1-butyl-3-methylimidazolium |
| C ₆ mim | 1-hexyl-3-methylimidazolium |
| C ₈ mim | 1-octyl-3-methylimidazolium |
| C ₁₀ mim | 1-decyl-3-methylimidazolium |
| C ₁₂ mim | 1-dodecyl-3-methylimidazolium |
| C ₄ dmim | 1-butyl-2,3-dimethylimidazolium |
| C ₂ py | 1-ethylpyridinium |
| C ₄ mpy | 1-butyl-4-methylpyridinium |
| C ₄ mpyr | 1-butyl-1-methylpyrrolidinium |
| P _{6,6,6,14} | Trihexyl(tetradecyl)phosphonium |
| C ₄ mim(ME) | 1-butyl-3-methylimidazolium 2-(2-methoxyethoxy) |
| C ₈ mim(ME) | 1-octyl-3-methylimidazolium 2-(2-methoxyethoxy) |

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