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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,

$$\delta^2 = \frac{\Delta H_v - RT}{V} \tag{1}$$

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];

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

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.

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

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 $MPa^{1/2}$) 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 [NTf_2], [PF_6], [BF_4] and [OTf] anion but not for [MSO_4], [OSO_4], [ESO_4(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) C_2mim; (b) C_4mim; (c) C_6mim; (d) C_8mim

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

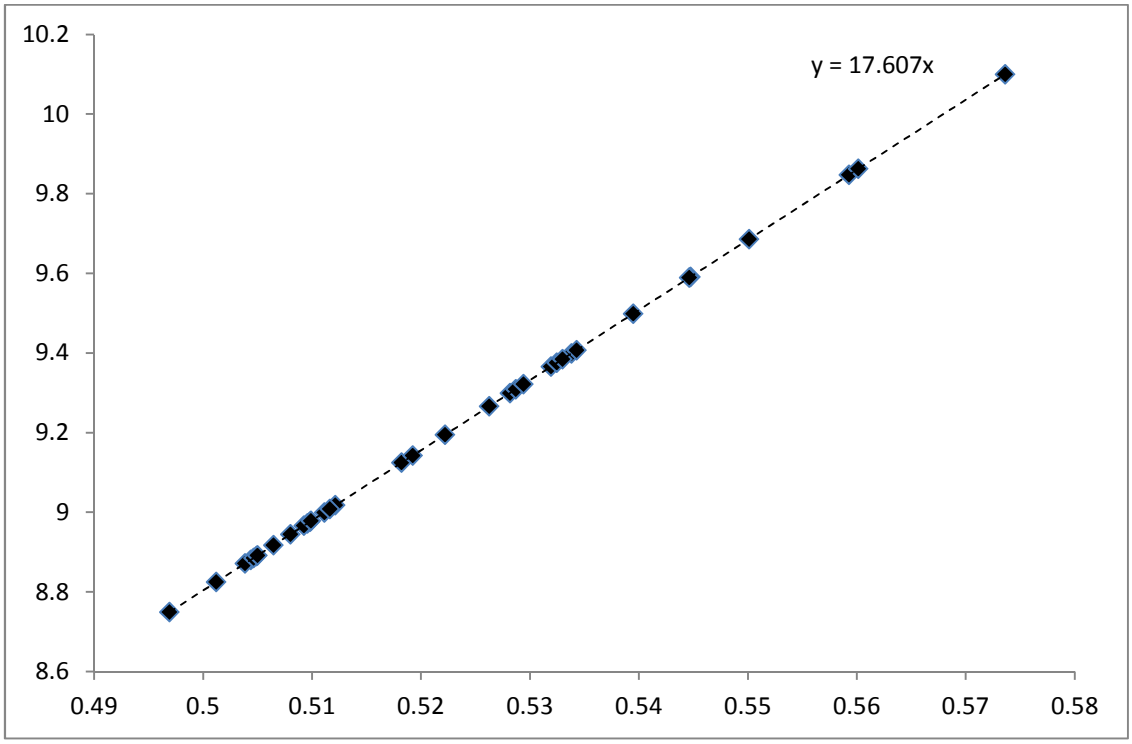


Figure 1: Solubility parameter, δ (cal. cm^{-3}) vs. LL for 35 ILs at 298.15 K

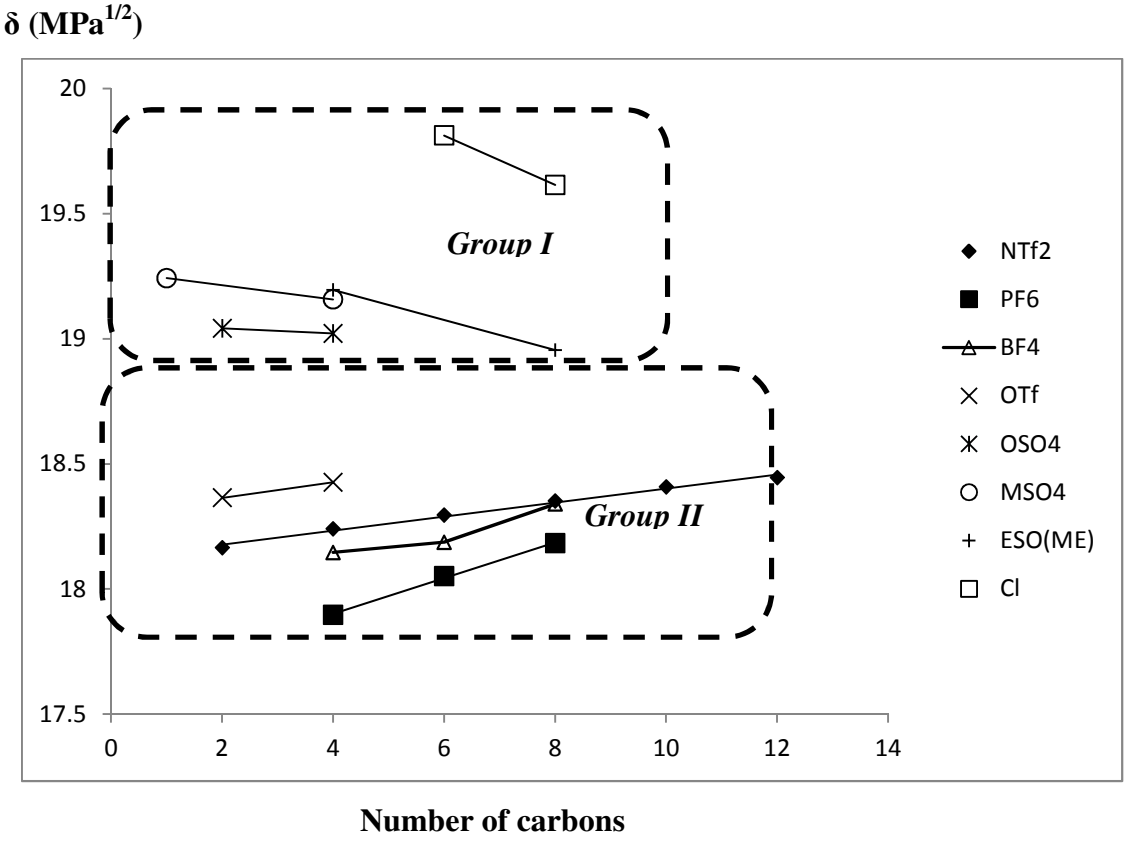
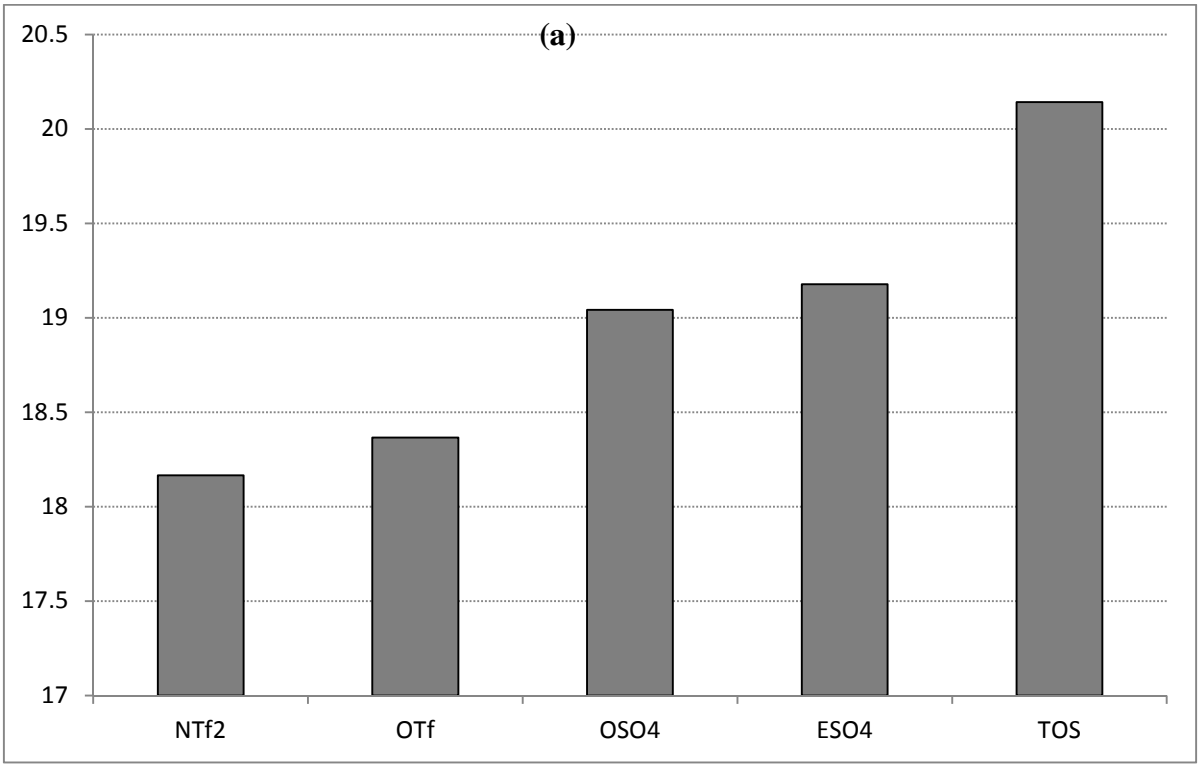


Figure 2: Solubility parameter, δ ($MPa^{1/2}$) as a function of the number of carbons in the alkyl side chain of imidazolium-based cation

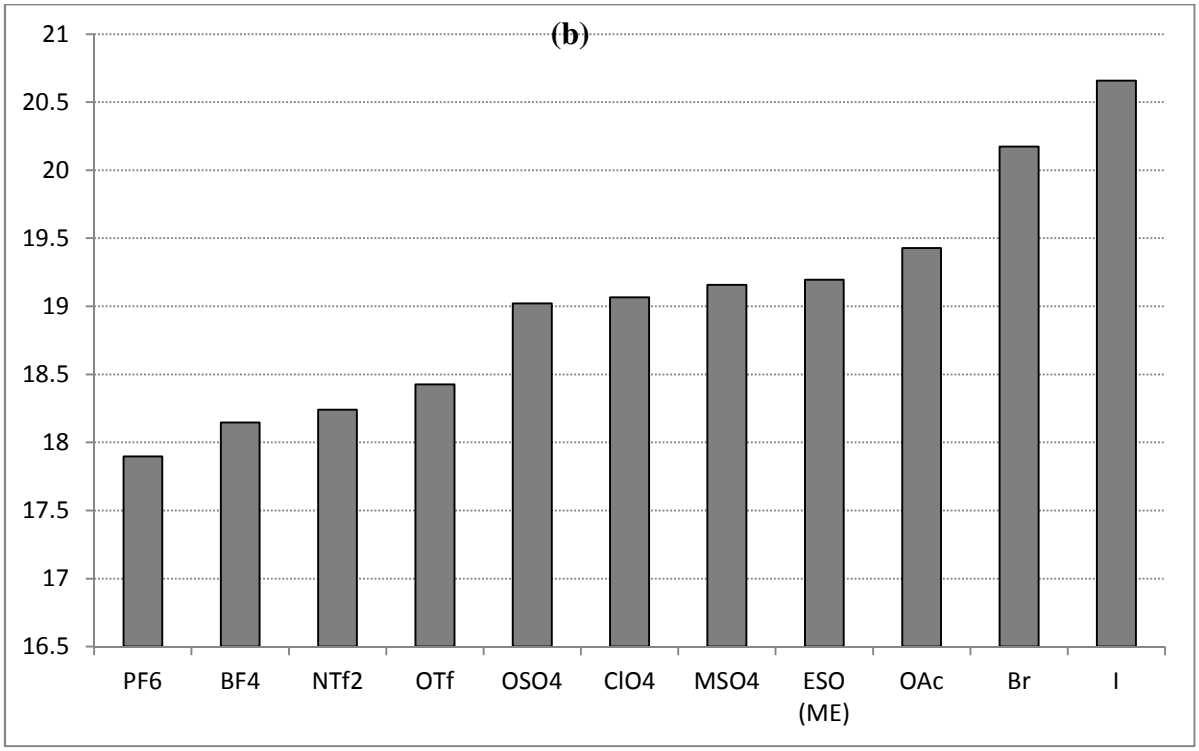
Group I : The solubility parameter, δ decrease with the number of carbons in the alkyl side-chain of imidazolium-based cation

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$^{1/2}$)



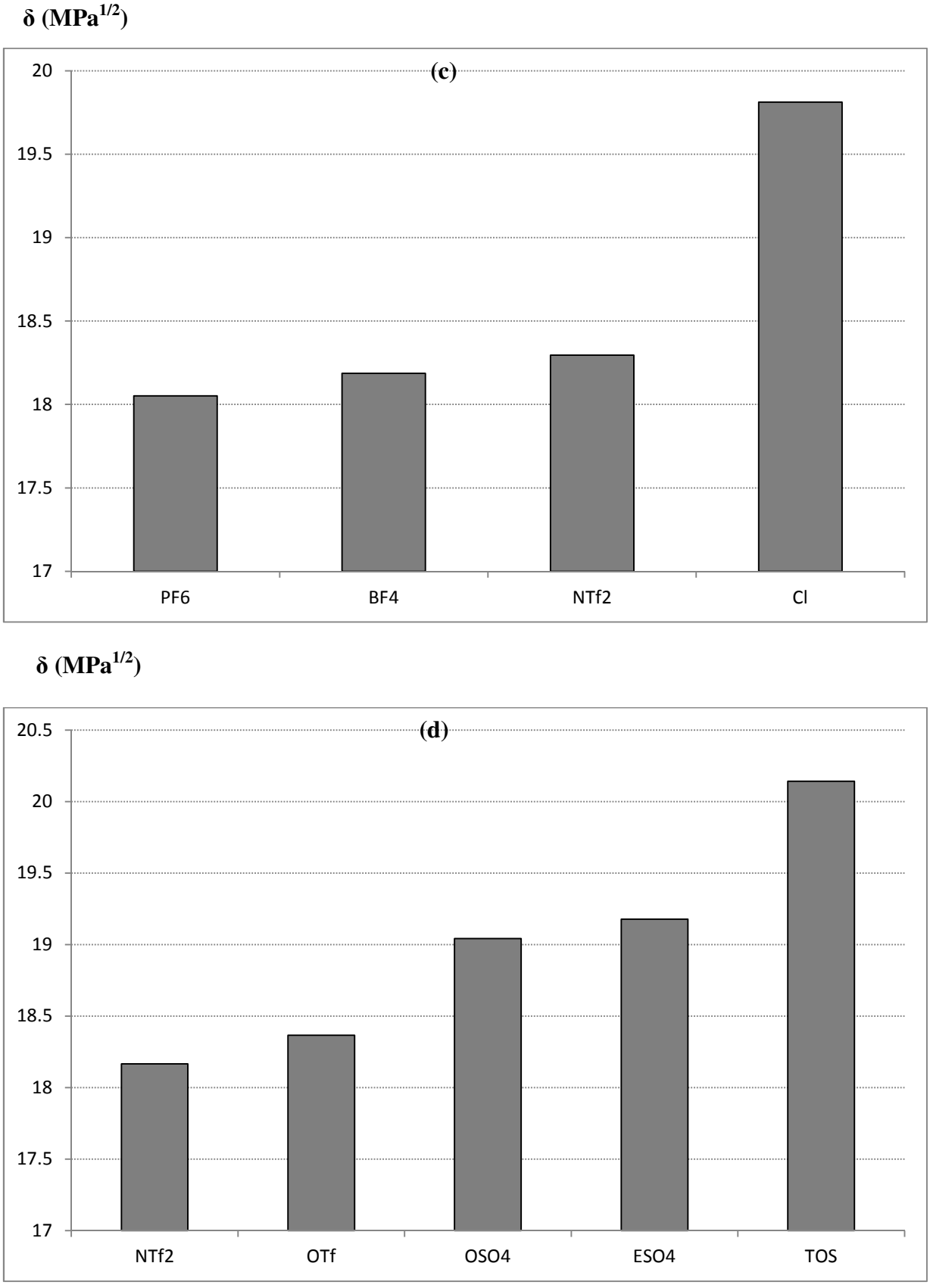


Figure 3: Anion influence on the solubility parameter, δ ($MPa^{1/2}$) for ILs based on: (a) C_2mim; (b) C_4mim; (c) C_6mim; (d) C_8mim

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_2mim NTf_2	18.165	C_2mim OTf	18.364
C_4mim NTf_2	18.240	C_4mim OTf	18.426
C_6mim NTf_2	18.296	$P_{6,6,6,14}$ OTf	18.807
C_8mim NTf_2	18.352	C_2mim OSO_4	19.041
C_{10}mim NTf_2	18.408	C_4mim OSO_4	19.021
C_{12}mim NTf_2	18.445	C_1mim MSO_4	19.242
C_4mpyrr NTf_2	18.175	C_4mim MSO_4	19.157
$P_{6,6,6,14}$ NTf_2	18.663	C_4mim OAc	19.429
C_4mim BF_4	18.146	$P_{6,6,6,14}$ OAc	19.226
C_6mim BF_4	18.187	C_2mim ESO_4	19.177
C_8mim BF_4	18.340	C_2py ESO_4	19.618
C_4dmim BF_4	18.360	C_4mim(ME) ESO_4	19.195
C_4mpy BF_4	18.701	C_8mim(ME) ESO_4	18.954
C_4mim PF_6	17.897	C_6mim Cl	19.812
C_6mim PF_6	18.051	C_8mim Cl	19.614
C_8mim PF_6	18.183	C_4mim I	20.659
C_4mim ClO_4	19.067	C_4mim Br	20.173
C_2mim 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_2mim NTf_2	18.165	27.6[1]	-	38.4[24]	-
C_4mim NTf_2	18.240	26.7[1]	-	-	25.5[25]
C_6mim NTf_2	18.296	25.6[1]	20.25[2]	-	-
C_8mim NTf_2	18.352	25.0[1]	-	-	-
C_4mim BF_4	18.146	31.6[1]	24.3[3]	47.4[24]	-
C_6mim BF_4	18.187	-	23.3[3]	-	-
C_8mim BF_4	18.340	-	22.5[3]	-	-
C_4mim PF_6	17.897	29.8[1]	-	43.8[24]	30.2[25]
C_6mim PF_6	18.051	28.6[1]	-	-	-
C_8mim PF_6	18.183	27.8[1]	-	-	-
C_2mim OTf	18.364	-	-	47.2[24]	-
C_4mim OTf	18.426	24.9[1]	22.67[2]	-	25.4[25]
C_4mim OSO_4	19.021	-	22.83[2]	-	-
C_8mim 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_1mim	1,3-dimethylimidazolium
C_2mim	1-ethyl-3-methylimidazolium
C_4mim	1-butyl-3-methylimidazolium
C_6mim	1-hexyl-3-methylimidazolium
C_8mim	1-octyl-3-methylimidazolium
C_{10}mim	1-decyl-3-methylimidazolium
C_{12}mim	1-dodecyl-3-methylimidazolium
C_4dmim	1-butyl-2,3-dimethylimidazolium
C_2py	1-ethylpyridinium
C_4mpy	1-butyl-4-methylpyridinium
C_4mpyrr	1-butyl-1-methylpyrrolidinium
$P_{6,6,6,14}$	Trihexyl(tetradecyl)phosphonium
C_4mim(ME)	1-butyl-3-methylimidazolium 2-(2-methoxyethoxy)
C_8mim(ME)	1-octyl-3-methylimidazolium 2-(2-methoxyethoxy)

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