

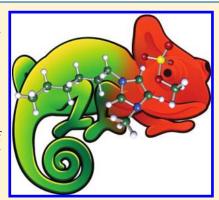
Chameleonic Behavior of Ionic Liquids and Its Impact on the Estimation of Solubility Parameters

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ABSTRACT: The possibility of developing a scale for solubility parameters, with the purpose of predicting the performance and aiding the selection of ILs, was evaluated. For the estimation of solubility parameters, infinite-dilution activity coefficient data were used. The results allowed the identification of a curious behavior for ILs that seem to present more than one solubility parameter, acting as polar molecules in some situations and as nonpolar molecules in others, depending on the medium. This behavior was confirmed by solubility measurements of $[C_4MIM][PF_6]$ in solvent mixtures. In this work, the solubility parameters were also estimated from other properties, namely, viscosities and enthalpies of vaporization, and the relation between the various sets of solubility parameters is discussed. The results obtained suggest that, given the complexity of IL molecules and their liquid phases, a one-dimensional scale for solubility parameters that is able to characterize these fluids is not feasible.



■ INTRODUCTION

Ionic liquids (ILs) are novel solvents with unique characteristics that make them feasible candidates for use in separation, synthesis, catalysis, and electrochemistry processes. They are salts with low melting points (<100 °C), negligible vapor pressures, and good thermal stabilities; they are nonflammable; and they have solvation abilities for wide ranges of compounds, including organic and inorganic compounds and even biopolymers that are soluble in few other solvents. 1-3 The possibility of fine-tuning their properties, through the combination of cations and anions, allows the design of task-specific ILs intended for a specific application. ⁴ The structure—property relationship of ILs has been subject of intense research, with the aiming of better understanding how the structure of an IL influences its physical and chemical properties. 2,5,6 For that purpose, both group contribution methods and QSAR/QSPR (quantitative structureactivity/-property relationships) approaches have been proposed for the prediction of the thermophysical properties, $^{1,2,4,\frac{1}{7}-13}$ phase behaviors, ^{14–18} and toxicities of ILs. ¹⁹ Another approach that has proved useful in the prediction of solubility relations for the past decades is the use of solubility parameters. 20

The solubility parameter is a concept that has been used for many years to select solvents; ^{20,21} predict the compatibility of polymers, resins, and plasticizers; ²⁰⁻²² prepare formulations in the paint industry; ^{20,21} design drug-delivery systems; ^{23,24} and generally understand the interactions between solutes and solvents. Compounds with similar solubility parameters are, in principle, miscible, although a few notable exceptions for highly

fluorinated molecules can occur. Extensive tables of solubility parameters can be found in the literature for ordinary solvents and materials. A few attempts to apply this concept to ionic liquids have been reported. The most fundamental approach would be to use the enthalpies of vaporization for their estimation. However, because IL volatilities are very low and because information concerning their enthalpies of vaporization is scarce and unreliable, ^{36,37} various authors have attempted to use other properties to predict solubility parameters. Camper et al.²⁸ estimated solubility parameters from melting points, but because few ILs present a well-defined melting temperature, this approach turned out to be of limited utility. The same author used values of lattice energy density²⁷ by applying the Kapustinskii equation (whereby lattice energy is estimated using the charges and molar radii of the ions and ignoring ion polarity). Kilaru et al.30 used values of surface tension to estimate the solubility parameters; however, the resulting correlation depends on the components (gas and type of IL), which severely restricts its application. Later, Kilaru et al. 31 based their solubility-parameter scale on the free energy of activation from viscosity data using Eyring's absolute reaction rate theory. 31 Recently, using the same approach, Moganty et al.³⁸ estimated solubility parameters by applying a new relation between the free energy of activation of viscosity and the energy of vaporization. Lee and Lee³² estimated

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IL solubility parameters using intrinsic viscosities, which, although time-consuming, is a more fundamentally sound approach. Another approach to estimate the solubility parameters is based on phase equilibrium data. Solubility ^{24,26,29,35} or infinite-dilution activity coefficients can be used to estimate the solubility parameters. Mutelet et al. ³⁴ estimated the solubility parameters from activity coefficients at infinite dilution obtained by inverse gas chromatography (IGC). Recently, Marciniak ³³ proposed an alternative approach to the estimation of solubility parameters using this type of data. The various approaches give contradictory results for the solubility-parameter values, and no comprehensive study of a wide range of ILs or comparison of solubility-parameter estimation approaches has been carried out.

This work aims to evaluate the possibility of creating a solubility-parameter scale for ILs that can enable the design and selection of the most suitable IL for a specific purpose. Different approaches for the estimation of solubility parameters are compared and discussed. It is shown that the complexity of ILs, which confers their peculiar and interesting properties, hinders the development of a one-dimensional solubility-parameter scale.

■ ESTIMATION OF IONIC LIQUID SOLUBILITY PARAMETERS

The solubility-parameter concept was initially defined by Hildebrand and Scott as the square root of the cohesive energy density, which is the ratio of the energy of vaporization $(\Delta_{\rm vap} U)$ to the molar volume $(V)^{20,21,39}$

$$\delta = \left(\frac{\Delta_{\text{vap}}U}{V}\right)^{1/2} \tag{1}$$

Because $\Delta_{\rm vap}U=\Delta_{\rm vap}H-RT$ for most solvents, solubility parameters can be estimated from knowledge of the enthalpies of vaporization. Unfortunately, this is particularly difficult for ILs because their volatilities are very low and data on their enthalpies of vaporization are scarce and unreliable. 5,36,37

The solubility parameter is the basis for the excess Gibbs energy model proposed by Scatchard and Hildebrand²¹ known as regular solution theory. According to this theory, for systems that have negligible excess volume and entropy^{20,21,39}

$$G^{E} = U^{E} = \phi_{i}\phi_{j}(\delta_{i} - \delta_{j})^{2}(x_{i}V_{i} + x_{j}V_{j})$$
(2)

Using this relationship and classic thermodynamic approaches, it is possible to calculate the infinite-dilution activity coefficient, γ^{∞} , as

$$RT \ln(\gamma_j^{\infty}) = V_j (\delta_i - \delta_j)^2$$
 (3)

where i refers to the IL and j refers to a solvent with a known solubility parameter, δ_j . From this relation, the IL's solubility parameter, δ_i can be estimated from the values of the solvent's solubility parameter, δ_j and molar volume, V_j . This relation is particularly useful because, unlike for heats of vaporization, there are plenty of infinite-dilution activity coefficients data available in the literature for a large set of solvents in a wide number of ILs.

Viscosities, ^{31,32,38} surface tensions, ³⁰ lattice energy densities, ²⁷ and melting points ²⁸ are other properties that can be used to estimate solubility parameters. Viscosity is particularly interesting, as a large body of experimental data with adequate quality is

available for ILs. Kilaru and Scovazzo³¹ proposed the estimation of solubility parameters using viscosity data as

$$\delta_i = \left\{ \frac{K_{\rm v}RT}{V_i} \ln \left[\frac{(1 \times 10^{-9})\mu_i V_i}{h N_{\rm A}} \right] \right\}^{1/2} \tag{4}$$

where μ is the IL's dynamic viscosity, h is the Planck constant, $N_{\rm A}$ is Avogadro's number, V is the molar volume, and $K_{\rm v}$ is a proportionality constant. The aforementioned approaches using enthalpies of vaporization, infinite-dilution activity coefficients, and viscosities were applied here to estimate the solubility parameters of ILs.

■ EXPERIMENTAL METHODS

Materials. The ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIM][PF_6]$), water, 1-propanol, and toluene were used in the solubility study of ionic liquids in mixed solvents. The IL was acquired from IoLiTec with a mass-fraction purity of >99% and bromide impurities of <85 ppm. The water was doubly distilled, passed through a reverse osmosis system, and further treated with a Milli-Q plus 185 water purification apparatus. It had a resistivity of 18.2 $M\Omega \cdot cm$ and a total organic carbon content of less than 5 $\mu g \cdot L^{-1}$ and was free of particles greater than 0.22 μm . Toluene was acquired from BDH Prolabo with a purity of >99%. 1-Propanol was obtained from Lab-Scan Analytical Sciences with a purity of >99.5%.

Experimental Procedure. To measure IL solubilities in mixed solvents, samples at various compositions of the two volatile components were prepared by weight, mixed by vigorous stirring with excess pure ionic liquid, and allowed to reach equilibrium by phase separation in 22 mL glass vials for at least 48 h at 298.15 K. The minimum time period to reach equilibration was verified in previous studies. 40–44 These conditions were selected to ensure that no degradation of the PF₆ anion in the aqueous solutions occurred. 45 The temperature was maintained by keeping the glass vials containing the phases in equilibrium inside an aluminum block placed in an air bath, specially designed for this purpose. 40,41 A Julabo circulator (model F25-HD) coupled to the system that allowed the passage of a thermostatic fluid around the aluminum block maintained the system temperature within ± 0.01 K by means of a proportional—integral—derivative (PID) temperature controller driven by a calibrated Pt(100) temperature probe inserted directly into the aluminum block.

The solubilities of the ILs in the propanol—water-rich phase were measured using a Shimadzu UV-1700 Pharma-Spec spectrophotometer. Samples of 0.5 g were taken and diluted by a factor ranging from 0.5:250 to 0.5:25000 (v/v) in ultrapure water. The maximum absorbance for the imidazolium cation was previously established to be at a wavelength of 211 nm. ¹⁶ The solubility results as a function of composition were measured at 298.15 K and atmospheric pressure. Averages of at least five independent measurements were obtained, and the composition was determined by means of a previously determined calibration curve.

For the toluene–1-propanol mixtures, samples of 0.1–2 g taken from the solvent-mixture-rich phase were weighed, and the volatile solvents were removed by evaporation under a moderate vacuum (1 Pa) in a glass flask designed for this purpose. The IL content was determined by weight. For each composition, at least three individual measurements were performed. All massfraction quantifications were performed gravimetrically with a precision of $\pm 10^{-4}~{\rm g}$ at 298 K.

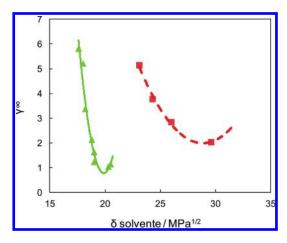


Figure 1. Activity coefficients at infinite dilution for $[C_4MIM][PF_6]$ in a series of solvents expressed as a function of the solvent solubility parameters. ^{21,34}

■ RESULTS AND DISCUSSION

Chameleonic Behavior of Ionic Liquids. In addition to the three methods for the estimation of solubility parameters described above, another approach often used consists of plotting the solubility of the target compound against the solubility parameters of a range of solvents or solvent mixtures in which the solubility has been measured. ^{24,26,29,35} The solubility parameter of the target compound corresponds to the maximum of the solubility curve. For poorly miscible liquids, the solubility (x) can be related to the infinite-dilution activity coefficient by

$$\gamma^{\infty} = \frac{1}{x} \tag{5}$$

A similar approach for the estimation of the solubility parameter can thus be achieved by plotting the infinite-dilution activity coefficient against the solubility parameter for a series of solvents and identifying the target-compound solubility parameter from the function minimum. If this approach is applied for ILs using the available infinite-dilution activity coefficients, the picture that emerges, shown in Figure 1 for [C₄MIM][PF₆], is quite surprising. Similar results were obtained for other ILs, as shown in Figures S1 and S2 (Supporting Information) for [C₄MIM][BF₄] and [C₂MIM][NTf₂], respectively. The results clearly suggest the presence of a double minimum: one at solubility parameters of around 20 MPa^{1/2} for nonpolar solvents interacting with the IL through dispersion forces and another at solubility parameters of around 30 MPa^{1/2} for polar solvents interacting with the IL through dipoles and hydrogen bonding, such as alcohols. Such double peaks, which suggest that the compound can be described by two different solubility parameters, have been observed for other complex molecules such as drugs, ^{24,26,29,35} and it was named chameleonic behavior by Hoy. 46 It results from the ability of a molecule to interact differently depending on the environment type. This behavior, which can be understood as a sort of amphiphilic character, is what confers a special solvation ability to ILs, allowing them to solubilize a wider range of compounds than

To confirm the chameleonic behavior observed in Figure 1, the solubilities of $[C_4MIM][PF_6]$ in mixed solvents (1-propanol—water and 1-propanol—toluene) were measured. The results, expressed as a function of the solvent-mixture solubility parameters,

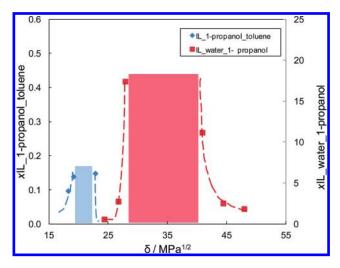


Figure 2. Solubilities of $[C_4MIM][PF_6]$ in water-1-propanol and 1-propanol—toluene mixtures expressed as a function of the solubility parameters of the solvent mixtures. Lines are guides to the eye.

can be estimated as

$$\delta = \sum \phi_i \delta_i \tag{6}$$

where δ_i is the solubility parameter of the pure solvents and ϕ_i is their volume fraction in the mixture.

Propanol—water mixtures reproduce the polar environment of polar solvents, whereas propanol—toluene mixtures allow for the study of nonpolar environments. In each solvent mixture, it was possible to identify a region of complete miscibility, confirming that this ionic liquid is fully miscible with both polar and nonpolar solvents. The region of complete miscibility, colored in Figure 2, is in good agreement with the minima obtained from the infinite-dilution activity coefficients presented in Figure 1. (Data for the two mixtures are reported in Tables S1 and S2 of the Supporting Information.)

Using molecular dynamics simulations, Canongia Lopes et al. and Canongia Lopes and Pádua ^{47,48} showed that ionic liquids are nanostructured fluids in which the ion pairs arrange themselves into polar and nonpolar domains. They later showed that the solvation of compounds in ionic liquids changes with the nature of the solute: polar compounds are preferentially solvated in the polar domains, whereas nonpolar compounds are solvated in the nonpolar domains. 49 It is this nanostructured nature of ionic liquids that confers their differentiated solvation abilities, allowing polar and nonpolar solute molecules to interact with the same solvent in regions with different natures as if they were interacting with two different molecules, giving rise to the odd solubility and solubility parameter behaviors discussed above. The chameleonic behavior observed through the solubility and infinite-dilution activity coefficients can thus be understood as an expression of the nanostructured nature of ionic liquids that gives them an amphiphilic character. It is this aspect that grants them a special solvation ability, allowing for the solubilization of a wider range of compounds than common solvents.

Estimation of Solubility Parameters from Infinite-Dilution Activity Coefficients. Activity coefficients at infinite dilution, measured by inverse gas chromatography (IGC), are available in the literature for a large number of solvents in ILs, as listed in Table 1. For the estimation of IL solubility parameters using activity coefficients at infinite dilution in this work, it was taken

Table 1. Nonpolar (δ_{NP}) and Polar (δ_P) Solubility Parameters for Different ILs at 298.15 K^a

101 Different ILS at 25	, 0, 13 IC		
IL	$\gamma_{ m max}^\infty - \gamma_{ m min}^\infty$	$\delta_{ m NP}$ (MPa $^{1/2}$)	$\delta_{ ext{P}}$ (MPa $^{1/2}$)
$[C_2MIM][NTf_2]$	$65.3 - 1.05^{34,53-56}$	22.55	29.22
$[C_2MIM][BF_4]$	201-1.11 ^{57,58}	23.97	_
$[C_2MIM][CF_3SO_3]$	$166 - 1.07^{59}$	23.96	_
$[C_2MIM][SCN]$	$434 - 1.21^{60}$	25.27	30.51
$[C_2MIM][EtSO_4]$	$227 - 1.05^{55,61}$	24.53	30.96
$[C_2MIM][TFA]$	$193 - 2.75^{62}$	24.29	_
$[C_2MIM][FAP]$	$33.0 - 1.06^{63}$	21.54	28.68
$[C_2MIM][B(CN)_4]$	$58.9 - 1.05^{64}$	22.21	30.54
$[C_2MIM][Tosylate]$	$78.1 - 1.54^{65}$	23.59	_
$[C_4MIM][NTf_2]$	$45.1 - 1.06^{55,66-68}$	21.73	29.32
$[C_4MIM][BF_4]$	$240\!-\!1.00^{58,66,69-71}$	23.71	30.47
$[C_4MIM][PF_6]$	$8.17 - 1.03^{34,72,73}$	22.32	29.02
$[C_4MIM][MeSO_4]$	$1.68 - 1.21^{72}$	_	31.92
$[C_4MIM][CF_3SO_3]$	$87.2 - 1.02^{74 - 78}$	23.21	31.10
$[C_4MIM][SCN]$	$350 - 1.08^{79}$	24.47	33.24
$[C_4MIM][C_8H_{17}SO_4]$	$10.3 - 1.05^{65,80}$	21.08	_
$[C_6MIM][NTf_2]$	$34.7 - 1.04^{72,81}$	20.89	31.01
$[C_6MIM][BF_4]$	$69.6 - 11.4^{70,82}$	23.08	_
$[C_6MIM][PF6]$	$44.6 - 1.03^{83}$	21.95	_
$[C_6MIM][CF_3SO_3]$	$27.2 - 1.43^{78,84}$	22.49	_
$[C_6MIM][SCN]$	$95.7 - 1.07^{85}$	23.36	_
$[C_8MIM][NTf_2]$	$6.82 - 1.03^{67}$	20.74	31.36
$[C_8MIM][BF_4]$	$16.7 - 1.10^{58,66}$	21.80	33.86
$[C_8MIM][Cl]$	$26.1 - 1.75^{86}$	22.50	_
$[C_8MIM][PF_6]$	$18.0 - 1.02^{87}$	21.54	_
$[C_8MIM][CF_3SO_3]$	$12.6 - 4.53^{86}$	21.54	_
$[C_{16}MIM][BF_4]$	$2.44 - 1.01^{88}$	19.41	28.96
$[C_6OC_1C_1IM][NTf_2]$	$13.6 - 1.03^{89}$	21.13	30.13
$[(C_6OC_1)_2IM][NTf_2]$	$4.80 - 1.00^{89}$	19.82	31.67
$[MMIM][MeSO_4]$	$301 - 5.93^{90}$	25.50	_
$[C_6 0_2 C_1 IM][Br]$	$190 - 1.12^{65}$	25.23	_
$[C_{10}O_2C_1IM][Br]$	$115 - 1.53^{65}$	23.46	_
$[C_2C_1C_1IM][NTf_2]$	$55.4 - 1.07^{54}$	22.80	29.41
$[C_3C_1C_1IM][BF_4]$	$8.86 - 1.40^{91}$	26.46	26.41
$[C_2py][NTf_2]$	$79.9 - 1.00^{90}$	22.45	29.53
$[C_4Mpy][NTf_2]$	$28.3 - 1.00^{67,92}$	21.91	30.38
$[C_4Mpy][BF_4]$	129-1.08 ^{53,93,94}	23.71	29.89
$[C_4Mpy][CF_3SO_3]$	49.6-1.00 ⁹⁵	22.48	_
$[C_4MpyR][NTf_2]$	$28.3 - 1.50^{67}$	22.41	_
$[C_4MpyR][CF_3SO_3]$	$71.5 - 1.00^{96}$	23.14	31.07
$[C_4MpyR][BF_4]$	143-1.03 ⁵⁶	23.68	29.85
$[C_6MpyR][NTf_2]$	15.7-4.45 ⁹⁷	21.23	_
$[C_8MpyR][NTf_2]$	8.78-3.11 ⁹⁷	20.76	_
[tri-iso-BMP][Tosylate]	$61.4 - 1.20^{98}$	22.33	_
[tri-BMP][MeSO ₄]	17.3-1.00 ⁹⁹	21.55	_
[THTDP][NTf ₂]	$1.55 - 1.00^{100}$	17.06	30.34
$[N_{1114}][NTf_2]$	$45.4 - 1.02^{101}$	22.33	31.16
$[N_{1888}][NTf_2]$	$1.53 - 1.00^{102}$	16.95	_
[S ₂₂₂][NTf ₂] ^a Pange of activity coefficients	36.9-1.00 ¹⁰³	22.19	29.63

^a Range of activity coefficients at infinite dilution reported depends on literature availability.

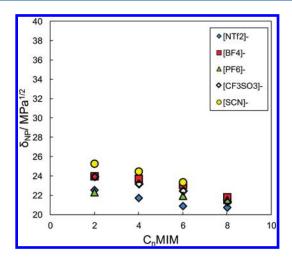


Figure 3. Effect of the alkyl-chain length on δ_{NP} for $[C_nMIM][X]$.

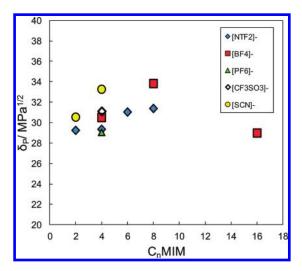


Figure 4. Effect of the alkyl-chain length on δ_P for $[C_nMIM][X]$. For the cations $[C_6MIM]^+$ and $[C_{16}MIM]^+$, only one value was estimated.

into account that, as previously discussed, the ILs present two, rather than one, solubility parameters: one representing its non-polar character (nonpolar solubility parameter, $\delta_{\rm NP}$) and another representing its polar character (polar solubility parameter, $\delta_{\rm P}$).

For the estimation of the nonpolar solubility parameter, $\delta_{\rm NP}$, eq 3 was applied, based on the infinite-dilution activity coefficients of nonpolar solvents, with δ_j below 23 MPa $^{1/2}$. The values of the solvent solubility parameters and molar volumes were collected from the literature 21 and are reported in Table S3 of the Supporting Information. For each IL, a single, temperature-independent solubility parameter was estimated using all of the available information through the minimization of the following objective function (OF)

$$OF = \sum_{i} (\delta_{NP} - \delta_{i})^{2}$$
 (7)

where δ_{NP} is the nonpolar IL solubility parameter and δ_i is the IL solubility parameter estimated for each solvent by eq 3. The values estimated for the nonpolar (δ_{NP}) solubility parameters are reported in Table 1.

The polar solubility parameters, δ_P , were estimated from data for polar solvents with δ_i above 23 MPa^{1/2}. These were essentially

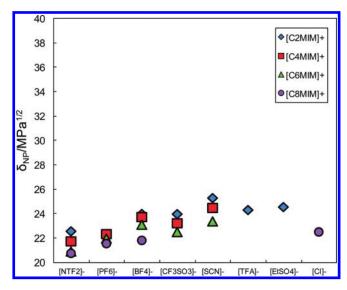


Figure 5. Effect of the anion on the nonpolar solubility parameters for $[C_nMIM]^+$. The anions are ordered in terms of increasing solvatochromic parameter β .

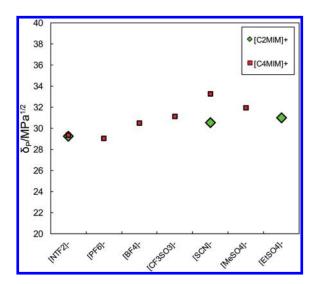


Figure 6. Effect of the anion on the polar solubility parameters for $[C_nMIM]^+$. The anions are ordered in terms of increasing solvatochromic parameter β .

alcohols, and in many cases, the infinite-dilution activity coefficients presented negative deviations from ideality that could not be described by eq 3, so that the approach used for the estimation of the nonpolar (δ_{NP}) solubility parameters was not applicable. Therefore, the solubility parameter for each polar compound was estimated through the identification of the minimum in a plot of activity coefficients at infinite dilution as a function of solubility parameter for polar solvents, as represented by the dashed line in Figure 1. The values estimated for the polar solubility parameters (δ_P) are also reported in Table 1. Figures 3 and 4 depict the nonpolar and polar solubility parameters, respectively, for ILs with a common anion as functions of the cation alkyl-chain length. As can be observed in Figure 3, the nonpolar solubility parameters decrease with increasing alkyl-chain length, indicating that an increase in the alkyl-chain length enhances the IL nonpolar character, as expected. However, such behavior was not

observed in Figure 4, because the alkyl chain does not play a role in the solvation of solutes in the polar domain, so that the polar solubility parameter must thus, to a fair extent, be independent of the cation alkyl-chain length.

The nonpolar and polar solubility parameters for ILs with a common cation are plotted as functions of the anion polarity in Figures 5 and 6, respectively. In these plots, the anions are listed in ascending order of the solvatochromic parameter β , which describes the hydrogen-bond-accepting ability of the anion, as proposed by Lungwitz et al. Figure 5, it can be observed that the nonpolar solubility parameters increase with the anion's polarity, because more polar anions confer a more polar character on the IL, increasing its solubility parameter as expected. Similar behavior can be observed in Figure 6 for the polar solubility parameters. To confirm the reported results and to learn more about IL solubility parameters in order to clarify their complex behavior, attempts were made to estimate solubility parameters using other approaches, namely, viscosities and enthalpies of vaporization, as discussed previously.

Estimation of Solubility Parameters from Viscosity Data. The estimation of solubility parameters using eq 4 was carried out at 298.15 K. According to Kilaru et al.,³¹ the parameter K_v has a value of 7.8 for $[NTf_2]^-$ -based ionic liquids and a value of 6.4 for all remaining anions. The viscosity and density data used for solubility-parameter estimation are reported in Table 2.

Whereas the estimation of solubility parameters from infinite-dilution activity coefficients is based on data from binary systems and thus expresses solute—solvent interactions, solubility-parameter estimation based on viscosity data uses only data for a property of the pure IL, expressing the cation—anion and ion-pair interactions. Because the nature of the interactions is necessarily different in the two cases, different solubility-parameter scales will be obtained. Unlike the previous approach, the use of viscosities leads to a single solubility parameter, as reported in Table 2.

Effect of the Cation Alkyl-Chain Length on the Solubility **Parameters.** Figure 7 presents the solubility parameters for three families of ILs with a common anion as function of the cation alkyl-chain length. The first noticeable result is that the solubility parameters obtained from viscosity data are of the same order of magnitude as those previously obtained for polar solvents. Polar interactions, such as dipole-dipole, hydrogen-bonding, and Coulombic interactions, dominate the viscosity-related interactions. It is not surprising that a solubility parameter based on viscosities will express these types of interactions and will not be able to capture those related to dispersion forces, which dominate the nonpolar solubility parameters estimated from infinitedilution activity coefficients. The viscosity-based solubility parameters decrease with increasing cation alkyl-chain length, which corresponds to a decrease of the IL polar character. This decrease was found to be regular and identical for the three families of ILs investigated.

Effect of the Anion on the Solubility Parameters. Figure 8 shows the effect of the anion on the viscosity-based solubility parameters for three series of $[C_n MIM][X]$ ionic liquids with n ranging from 4 to 8. Unlike what was observed for the polar solubility parameters (δ_P) , the trend observed here was in good agreement with the expectations. The ionic liquids with hydrophilic anions were found to have higher solubility parameters than ILs with hydrophobic anions. As before, the solubility parameters are plotted in Figure 8 for the $[C_4MIM]^+$ cation as a function of increasing β solvatochromic parameter. So,51 Despite the

Table 2. Solubility Parameters and Viscosity and Density Data for Different ILs at 298.15 K^a

IL	$\mu_{ ext{max}} - \mu_{ ext{min}} \left(ext{mPa} \! \cdot \! ext{s} ight)$	$ ho~(\mathrm{g}\cdot\mathrm{cm}^{-3})$	δ (MPa $^{1/2}$
$[C_1MIM][NTf_2]$	$38.0 - 26.6^{104,105}$	1.57 ^{104,105}	28.17
$[C_2MIM][BF_4]$	$37.2 - 36.1^{106 - 108}$	$1.28^{106,109-113}$	31.32
$[C_2MIM][NTf_2]$	$34.7 - 24.5^{104,105,114-118}$	$1.52^{55,105,118-120}$	27.27
$[C_2MIM][CF_3SO_3]$	41.0 ¹²¹	$1.39^{122-124}$	28.87
[C ₂ MIM][EtSO ₄]	$100 - 95.0^{121,125 - 127}$	1.24 ^{125,126,128}	29.90
$[C_3MIM][NTf_2]$	45.7 ¹¹⁸	1.47 ¹¹⁸	26.99
$[C_4MIM][PF_6]$	$310 - 173^{3,105,116,129 - 137}$	$1.37^{130,134,138-142}$	29.98
$[C_4MIM][BF_4]$	$233 - 40.2^{3,105,107,133,143,144}$	1.20 ^{105,109,145,146}	30.41
$[C_4MIM][NTf_2]$	$69.0 - 20.7^{104,105,147,148}$	1.44 ^{55,116,149}	26.41
$[C_4MIM][CF_3SO_3]$	84.4 ¹⁰⁵	$1.30^{105,122-124}$	27.71
$[C_4MIM][CH_3CO_2]$	440 ¹¹⁵	1.05 ¹⁵⁰	32.11
[C ₄ MIM][MeSO ₄]	213 ¹⁵¹	1.21 ^{140,151}	29.87
$[C_4MIM][C(CN)_2]$	$31.8 - 14.6^{143,152}$	1.06^{152}	27.57
$[C_4MIM][C(CN)_3]$	27.4 ¹⁵²	1.05^{152}	26.40
$[C_5MIM][NTf_2]$	57.8 ¹¹⁸	1.39 ¹¹⁸	26.17
$[C_6MIM][PF6]$	$585 - 476^{3,114,134,148,153}$	$1.29^{10,139,140,142,154-156}$	28.81
$[C_6MIM][BF_4]$	$210 - 102^{114,157,158}$	1.15 ^{109,122,123,157}	28.59
$[C_6MIM][NTf_2]$	$71.5 - 53.5^{105,114,115,157,159}$	1.37 ^{105,159}	25.47
$[C_6MIM][Cl]$	$716 - 441^{3,160}$	$1.04^{161,162}$	31.92
$[C_7MIM][NTf_2]$	81.1 ¹¹⁸	1.35 ¹¹⁸	25.077
$[C_8MIM][PF_6]$	$886 - 682^{3,134,163-165}$	1.23 ^{134,139,140,142,155}	27.16
$[C_8MIM][BF_4]$	$360 - 324^{143,164,166-168}$	$1.10^{164,169-171}$	27.61
$[C_8MIM][NTf_2]$	97.8-90.0 104,105,172,173	$1.32^{36,170,173-175}$	24.67
[C ₈ MIM][Cl]	337 ³	1.01 ^{162,176}	29.05
$[C_8MIM][NO_3]$	664 ¹⁷⁷	1.06 ¹⁷⁷	29.10
$[C_{10}MIM][NTf_2]$	120 ¹¹⁸	1.28 ¹¹⁸	24.04
$[C_4py][BF_4]$	$163 - 160^{178,179}$	$1.21^{178,180}$	31.12
$[C_4py][NTf_2]$	60.0 ¹⁴⁷	1.45 ¹⁰⁵	26.80
$[C_4Mpy][BF_4]$	177 ¹¹⁵	1.18 ¹⁸¹	30.02
$[C_4MpyR][BF_4]$	$203 - 74.9^{105,143}$	1.39^{67}	24.47
[C ₄ MpyR][NTf ₂]	74.9 ¹⁰⁵	1.40 ¹⁸²	26.45
[THTDP][Cl]	2729 ¹⁸³	0.890^{183}	20.33
[THTDP][N(CN) ₂]	550 ¹⁸⁴	0.899^{152}	18.62

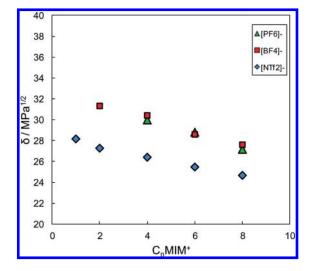


Figure 7. Effect of the alkyl-chain length on the viscosity-based solubility parameters for $[C_nMIM][X]$.

scattering observed, probably because of the irregular quality of the data, the expected general trend of $[CF_3SO_3]^- > [BF_4]^- > [PF6]^- > [NTf_2]^-$ was verified.

Estimation of Solubility Parameters from Vaporization Enthalpy Data. Recently, Rocha et al. ⁵² reported enthalpies of vaporization obtained from the measurement of vapor pressures using Knudsen effusion for the $[C_nMIM][NTf_2]$ series of ionic liquids with n ranging from 2 to 10. In the current work, those values were used to estimate solubility parameters according to eq 1, and the results are presented in Figure 9. Because of the limited amount of reliable data on enthalpies of vaporization available, it was possible to evaluate the effect of only the cation alkylchain length. In agreement with what was observed above, the solubility parameter was found to decrease with increasing chain length, that is, with increasing hydrophobicity of the ionic liquid.

Comparison between Methods. A comparison between the three methods for solubility-parameter estimation investigated in this work was carried out, to understand more about the nature of ionic liquids and the performance of various methods used.

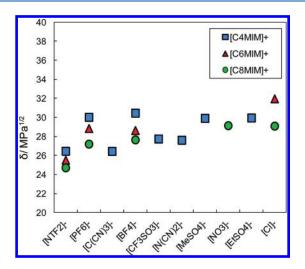


Figure 8. Effect of the anion family on the viscosity-based solubility parameters for $[C_nMIM][X]$. The anions are ordered in terms of increasing solvatochromic parameter β .

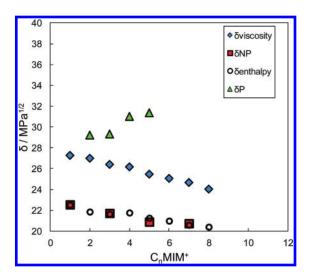


Figure 9. Comparison of the solubility parameters obtained by different estimation methods for the $[C_nMIM][NTf_2]$ series.

Because the enthalpy of vaporization data were available for only $[C_nMIM][NTf_2]$, the methods were compared for this series of ionic liquids, as presented in Figure 9.

In this figure, it can be observed that the nonpolar solubility parameter ($\delta_{\rm NP}$) and the solubility parameter from enthalpy of vaporization data are in close agreement. This results from the fact that, for these ionic liquids, the vaporization enthalpies are dominated by dispersion forces, as shown by Santos et al. ³⁷ This suggests that enthalpies of vaporization could be estimated from the solubility parameters obtained from infinite-dilution activity coefficients.

In contrast, as shown in Figures 7 and 8, the solubility parameters estimated from viscosity data have values closer to δ_P , which reflects the importance of polar and Coulombic interactions to the viscosities, as discussed by several authors.³¹

The results reported herein show that a single solubility parameter cannot be used to describe a complex compounds such as ionic liquids. Each approach for the estimation of solubility parameters emphasizes a specific aspect of the IL: the polar character

by the viscosity, the dispersive forces by the enthalpy of vaporization (although a different result could be obtained for other ionic liquids), and the nature of the solute probe and its solvation infinite-dilution activity coefficient. The conclusion seems to be that a one-dimensional solubility-parameter scale of the Hildebrand type is not capable of describing the behavior of ionic liquids. It is possible that a more complex approach than the Hansen type 20 might be adequate for that purpose, but this must be object of a future work. Based on the results presented in this work, we could nevertheless suggest that a double solubility-parameter scale, using $\delta_{\rm NP}$ and $\delta_{\rm P}$, could be used for specific purposes, such as solvent selection, when the polarity of the other compounds can be well-established and they are all of a single type (polar or nonpolar according to the definitions used in this work).

■ CONCLUSIONS

In this work, three approaches were used to estimate the solubility parameters of different ionic liquids, using data on activity coefficients at infinite dilution, viscosities, and enthalpies of vaporization.

The solubility parameters obtained from the activity coefficients at infinite dilution suggest that ionic liquids present a chameleonic behavior resulting from their amphiphilic character, allowing them to present differentiated solvation ability with solvents of different polarity interacting in different regions of the ionic liquid. An adequate description of an ionic liquid would require two solubility parameters: one for interactions with polar solvents and another for interactions with nonpolar solvents.

The solubility parameters obtained from viscosity data exhibited a behavior representative of stronger interactions, such as dipole—dipole, hydrogen-bonding, and Coulombic interactions. These solubility parameters present high values, closer to those obtained with polar solvents from the infinite-dilution activity coefficients.

Because of the lack of enthalpy of vaporization data, the three approaches were compared only for $[NTf_2]^-$ -based ionic liquids. The results showed that each approach provides different, although coherent, values for the solubility parameters that are representative of the different interactions that are involved in the properties used in their estimation.

The results reported herein indicate that complex molecules, such as ionic liquids, cannot be described by a one-dimensional solubility-parameter scale of the Hildebrand type. Nevertheless, it is suggested that the scales here reported could be derived and used with due care for specific applications with solvents of well-defined polarity.

ASSOCIATED CONTENT

Supporting Information. Graphics for different ionic liquids showing the chameleonic effect, collected data on the molar volume and solubility parameters of pure solvents, experimental solubility data for $[C_4MIM][PF_6]$ in mixtures of 1-propanol with toluene and 1-propanol with water. This material is available free of charge via the Internet at http://pubs.acs.org.

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