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Liquid–liquid miscibility and volumetric properties of aqueous solutions of ionic liquids as a function of temperature

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ABSTRACT

The volumetric properties of seven {water + ionic liquid} binary mixtures have been studied as a function of temperature from (293 to 343) K. The phase behaviour of the systems was first investigated using a nephelometric method and excess molar volumes were calculated from densities measured using an Anton Paar densimeter and fitted using a Redlich–Kister type equation. Two ionic liquids fully miscible with water (1-butyl-3-methylimidazolium tetrafluoroborate ($[C_1C_4Im][BF_4]$) and 1-ethyl-3-methylimidazolium ethylsulfate ($[C_1C_2Im][EtSO_4]$)) and five ionic liquids only partially miscible with water (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_1C_2Im][NTf_2]$), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_1C_4Im][NTf_2]$), 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_1C_4Im][PF_6]$), 1-butyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($[C_1C_4Pyrro][NTf_2]$), and butyltrimethylammonium bis(trifluoromethylsulfonyl)imide ($[N_{4111}][NTf_2]$)) were chosen. Small excess volumes (less than 0.5 $cm^3 \cdot mol^{-1}$ at 298 K) are obtained compared with the molar volumes of the pure components (less than 0.3% of the molar volume of the pure ionic liquid). For all the considered systems, except for {$[C_1C_2Im][EtSO_4]$ + water}, positive excess molar volumes were calculated. Finally, an increase of the non-ideality character is observed for all the systems as temperature increases.

1. Introduction

Ionic liquids (ILs) are considered as alternative media for a more sustainable chemical industry. Due to its specific properties and variety, this new class of liquids has received significant attention from research groups and industry for a range of novel applications including multiphasic catalysis and synthesis [1–4], separations [5–7], electrochemistry [8–10], lubrication [11], heat transfer [12], and analysis [13]. The generalised use of these new compounds needs an accurate knowledge of their physico-chemical properties both when pure and when they are mixed with molecular compounds, a probable scenario when ILs are considered as media to perform chemical reactions or implement new chemical processes.

The study of the physical chemistry of ionic liquids is crucial from a technological point of view but it also provides a better understanding of the mechanisms involved when using these new media. Given the huge number of possible combinations of anion and cation to form new ionic liquids [14], the experimental determination of the properties of all the ILs is not possible. Under these conditions, a better understanding of their physicochemical behaviour is necessary to predict their properties or at the very least provide general trends to enable rational use of this media. In other words, their unique potential can be linked to the development of predictive methods and/or computation researches [15,6,17–20]. For pure ILs, their properties are becoming increasingly available from both experimental and theoretical studies with the modeling and interpretation thereof being understood using molecular simulation tools. Even if accurate data are not always available, tendencies associated with, for example, the effect of changing the anion, the cation, presence of an aromatic cycle, length of the alkyl chain on the cation ring can generally be given. To date, only a relative small number of studies are available in the literature concerning the properties of binary systems composed of an IL and a molecular solvent.

In particular, only few data are available on the {IL + molecular component} (liquid + liquid) equilibria as a function of the temperature. Freire *et al.* [21–23] have reported the mutual miscibility of a bis(trifluoromethylsulfonyl)imide ($[NTf_2]^-$) based IL with water, using Karl–Fischer titration, on the temperature ranging from (288.15 to 318.15) K. The (liquid + liquid) equilibrium of the binary mixture {$[C_1C_4Im][PF_6]$ + water} is very well described as a function of the temperature and pressure in the literature [21,24–27]. This system was measured in the present study in order to quantify the uncertainty of the data presented, herein.

A closer analysis of the literature indicates that data on the volumetric properties of binary systems composed of an IL and water

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have only been published for hydrophilic ILs, for example 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_1C_4Im][BF_4]$) [28–32], 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ($[C_1C_1C_4Im][BF_4]$) [28], 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ($[C_1C_2Im][OTf]$) [33,34], 1-butyl-3-methylpyridinium tetrafluoroborate ($[C_1C_4py][BF_4]$) [35,36], 1-methyl-3-octylimidazolium chloride ($[C_1C_8Im]Cl$) [37], 1-hexyl-3-methylimidazolium chloride ($[C_1C_6Im]Cl$) [37], 1,3-dimethylimidazolium methylsulfate ($[C_1C_1Im][MeSO_4]$) [38], 1-butyl-3-methylimidazolium methylsulfate ($[C_1C_4Im][MeSO_4]$) [38], 1-ethyl-3-methylimidazolium ethylsulfate ($[C_1C_2Im][EtSO_4]$) [34,38–40], 1-ethyl-3-methylimidazolium trifluoroacetate ($[C_1C_2Im][TFA]$) [34]. The excess molar volumes calculated for all these systems are small compared with the molar volumes of the pure components (less than $1\ cm^3 \cdot mol^{-1}$), even less than $0.5\ cm^3 \cdot mol^{-1}$ for $[C_1C_1Im][MeSO_4]$, $[C_1C_4Im][MeSO_4]$, $[C_1C_2Im][EtSO_4]$, and $[C_1C_2Im][OTf]$. As a consequence, for practical purposes, the volumetric behaviour of these binary systems can be considered as ideal. Nevertheless, a more subtle analysis can provide pertinent information on the behaviour of these systems.

Asymmetric curves of the excess molar volume as a function of the composition are usually obtained for the aqueous solutions of IL which can be explained by the large molar volume difference between the two components. The maximum is generally observed in the water-rich region. However, for aqueous solutions of $[C_1C_2Im][OTf]$ [34] at 278 K, the maximum excess molar volume is obtained for a water mole fraction of 0.1 while at 348 K it is displaced into the water-rich region. The sign of the excess molar volumes and shape of the curve excess molar volume as a function of composition is mainly dependant on the anion of the IL [34]. For ionic liquids composed of the $[BF_4]^-$ anion ($[C_1C_4Im][BF_4]$, $[C_1C_1C_4Im][BF_4]$, and $[C_1C_4pyr][BF_4]$) over the temperature range considered (278 to 353) K, the excess molar volumes are positive with a slight increase with temperature. For $[C_1C_4Im][BF_4]$, maximum excess molar volumes of $0.5\ cm^3 \cdot mol^{-1}$ at 318 K are obtained. The $[OTf]^-$ based ionic liquids also leads to positive deviations from ideality, in general. For example, the system $\{[C_1C_2Im][OTf] + water\}$ [33,34] exhibits positive values for the excess molar volumes except at the lowest temperatures considered (278 to 298) K where negative values were calculated in the water-rich composition and positive values were calculated in the IL-rich composition, i.e. an S-shaped curve for the excess volume as a function of composition was found. Gomez *et al.* [37] studied ionic liquids based on the Cl^- anion also observed an S-shaped curve for the excess molar volumes as a function of the composition for the $\{[C_1C_8Im][Cl] + water\}$ and $\{[C_1C_6Im][Cl] + water\}$ binary mixtures but at temperatures up to 313 K.

The observed volumetric non-ideality, of the {IL + water} mixtures, increases with increasing temperature. Gomez *et al.* [37] attributed this behaviour to the balance between relative changes in hydrogen bonding and Coulombic interactions, as a function of temperature with the hydrogen bonding contribution becoming negligible at higher temperatures. The presence of an alkylsulfate anion generally leads to negative deviations to ideality [34,38,39]. Gomez *et al.* [39] and Rodriguez *et al.* [34] calculated, negative excess molar volumes except at the highest considered temperatures (up to 313 K) where slightly positive excess molar volumes were obtained in the water-rich region for the system $\{water + [C_1C_2Im][EtSO_4]\}$. Domanska *et al.* [38] studied $\{[C_1C_1Im][MeSO_4] + water\}$ at 298 K and observed negative excess molar volumes for ionic liquid mole fractions greater than 0.15 and slightly positive below this value. With increasing alkyl chain length on the imidazolium ring, *e.g.* for $\{[C_1C_4Im][MeSO_4] + water\}$, they observed negative values over the whole composition range at 298 K. Furthermore, over the temperature range (278 to 348) K, the system $\{[C_1C_2Im][TFA] + water\}$ Rodriguez *et al.* [34] showed negative excess molar volumes by over the whole composition range.

In contrast, no significant effect on the volumetric properties was observed when changing the alkyl chain length, for example in $\{[C_1C_6Im][Cl] + water\}$ compared with $\{[C_1C_8Im][Cl] + water\}$, [37] or when on replacing the hydrogen at the C(2) position on the imidazolium ring with a methyl group, for example comparing $\{[C_1C_4Im][BF_4] + water\}$ and $\{[C_1C_1C_4Im][BF_4] + water\ mixtures\}$ [28]. However, the presence of a pyridinium cation instead of an imidazolium cation slightly decreases the excess molar volume. At 298 K, the excess molar volume of the system $\{[C_1C_4Im][BF_4] + water\}$ presents a maximum of 0.48 for $x_{IL} = 0.45$ [29], while Ortega *et al.* [36] have measured an excess molar volume of 0.42 for $x_{IL} = 0.49$ for the system $\{[C_1C_4pyr][BF_4] + water\}$.

In this paper, the volumetric properties of {ILs + water} binary mixtures are studied on the basis of the excess molar volume. Water was chosen as it is often present in the IL samples and in the industrial mixtures. Two ILs totally miscible with water were considered, $[C_1C_4Im][BF_4]$ and $[C_1C_2Im][EtSO_4]$ as well as five ILs which are only partially miscible with water: $[C_1C_4Im][PF_6]$, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_1C_2Im][NTf_2]$), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_1C_4Im][NTf_2]$), 1-butyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($[C_1C_4Pyrro][NTf_2]$), butyltrimethylammonium bis(trifluoromethylsulfonyl)imide ($[N_{4111}][NTf_2]$).

Prior to the study the volumetric properties, the phase behaviour of the binary systems containing hydrophobic ILs was investigated in order to determine their mutual solubility with water. A nephelometric method [41,42] was used to detect cloud points. The volumetric properties are then investigated for IL mole fractions where only one liquid phase is observed. Excess molar volumes, defined as the difference between the actual molar volume of the mixture and that of an ideal solution at the same temperature, pressure, and composition, represent the deviation from the ideal behaviour of the mixtures. These values were calculated for all the {IL + water} mixtures from density measurements performed at atmospheric pressure as a function of temperature between (293 and 343) K at 5 K intervals and of the composition of the liquid mixture. In each case at least eight compositions for each binary system were examined.

2. Experimental

2.1. Materials

$[NTf_2]^-$ based ILs were prepared in house from the appropriate bromide salt using the procedure described by Bonhôte *et al.* [43] $[C_1C_2Im][EtSO_4]$, was prepared by reacting 1-methylimidazole with diethyl sulfate according to previously reported procedures by Xu *et al.* [44] $[C_1C_4Im][PF_6]$ and $[C_1C_4Im][BF_4]$ were purchased from Solvionic, with a minimum stated mole fraction purity of 0.999 and 0.98, respectively.

Prior to use, the halide and water contents of the ILs were determined. The chloride content was measured using suppressed ion chromatography (IC) [45]. The lithium content of the samples prepared from the lithium salt, was determined by inductively coupled plasma analysis (ICP) and the water concentration on the samples was determined before and after measurements by Coulometric Karl-Fischer titration using a Mettler Toledo DL32 titrator. The source, molar mass, halide, lithium, and water content of the ILs considered in this study, after drying under a pressure of 1 Pa at temperature 323.15 K for 15 h, are summarised in table 1.

TABLE 1

Molar mass (M^{IL}), chloride mass fraction content (w_{Cl}^{-}), lithium mass fraction content (w_{Li}^{+}), water content in mass fractions (w_w) and mole fractions (x_w) of ILs considered in this study.

Ionic liquid	$M^{IL}/(g \cdot mol^{-1})$	Source	$w_w \cdot 10^3$	$x_w \cdot 10^3$	$w_{Cl}^{-} \cdot 10^6$	$w_{Li}^{+} \cdot 10^6$ [a]
$[C_1C_2Im][NTf_2]$	391.31	QUILL	0.05	1.09	<5	2.59
$[C_1C_4Im][NTf_2]$	419.37		0.05	1.16	<5	0.74
$[N_{4111}][NTf_2]$	396.38		0.07	1.50	[b]	<5
$[C_1C_4Pyrro][NTf_2]$	422.41		0.05	1.20	<75	<5
$[C_2mim][EtSO_4]$	236.29		0.28	3.66	[b]	[c]
$[C_1C_4Im][PF_6]$	284.18	Solvionic	0.19	2.99	20	[c]
$[C_1C_4Im][BF_4]$	226.03		0.70	8.71	20	[c]

[a] Li^+ measured using ICP.

[b] Halogen free sample.

[c] Lithium free sample.

2.2. (Liquid + liquid) miscibility

The (liquid + liquid) miscibility gap was measured using a standard nephelometric method [41,42]. In this technique, the miscibility gap is determined by finding the temperature at which a phase change occurs in a mixture of hydrophobic IL and triply distilled water of known composition (gravimetrically determined). Prior to use, the water was first degassed and then introduced by gravity under its vapor pressure into a Schlenk tube containing the pure and dried ionic liquid. The relative uncertainty on the mass fraction is estimated to be less than $2 \cdot 10^{-4}$. All binary mixtures were placed in a thermostated equilibrium cell and brought to a temperature at which the mixture became homogeneous. Cloud point temperatures were visually determined by decreasing the temperature until the first droplet of the second phase appeared. By increasing the temperature, the clear-point temperature, *i.e.* temperature at which the mixture becomes entirely homogeneous, is determined in order to quantify the difference in the read-outs, which roughly characterizes the precision of the measurement. For measuring the temperature a 100 Ω platinum resistance thermometer (precision of ±0.05 K and accuracy of ±0.1 K) was used. Based on a statistical analysis of the present data, the uncertainty on the cloud-point is estimated as 0.5 K.

2.3. Preparation of the {IL + water} mixtures

After treating the ILs for 15 h at 323 K under vacuum (1 Pa), the samples were considered to be degassed and dry and were stored under a nitrogen atmosphere. Water was triply distilled and degassed by melting–freezing cycles while vacuum pumping non-condensable gases. The liquid mixtures $\{[C_1C_4Im][BF_4] + water\}$ and $\{[C_1C_2Im][EtSO_4] + water\}$ were prepared by mixing known quantities of IL and water in a syringe equipped with a Luer lock valve, to avoid any contact of the sample with atmosphere. The mixtures of a hydrophobic IL with water were prepared by saturating the treated IL with water until a second aqueous phase appeared and then putting this biphasic sample under vacuum to remove part of the water. Depending on the time under vacuum, different compositions were obtained. For all the mixtures, the water content was determined by coulometric Karl–Fischer titration using a Mettler Toledo DL32 titrator. The estimated uncertainty on the mole fraction composition of the mixture is less than 0.5%.

2.4. Determination of the molar volumes

The molar volume of the pure components and of the mixtures were calculated as a function of temperature from density measurements performed at atmospheric pressure between (293 and 343) K at 5 K intervals. All the density measurements were performed using a U-shape vibrating tube densimeter (Anton Paar, model DMA 512 P located at UBP, Clermont-Ferrand and Anton Paar, model 4500 located at QUB, Belfast) operating in a static mode. In both cases, temperatures were maintained to within ± 0.01 K as described in our previous papers [15]. The effect of the viscosity on the density measurement was taken into account. For $[C_1C_4Im][PF_6]$, which is the most viscous considered IL in this study (at 298 K, $\eta = 276$ cP) [46], the correction [47–49] affects the density by less than 0.1%. Hence, this correction was not considered in this work. The repeatability of the density measurements is $10^{-4}\ g \cdot cm^{-3}$. The results have an uncertainty [50,51] of $10^{-3}\ g \cdot cm^{-3}$. The compatibility of the two densimeters used in this work was checked using statistical methods (test of statistical hypothesis, comparison of two means) [52]. $[C_1C_2Im][NTf_2]$, whose density was measured with both densimeters [15], was considered for these statistical tests.

From the density of the mixtures as a function of composition and that of the pure components, it is possible to calculate the excess molar volume, V_m^E, of the mixtures by [53]

$$V_m^E = V_m^{mix} - \sum_i x_i \frac{M_i}{\rho_i}, \tag{1}$$

where V_m^{mix} is the molar volume of the mixture, x_i the mole fraction of component i with molar mass M_i, and density ρ_i.

The partial molar volume of each component of the mixture is defined as [53]:

$$V_{m,i} = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_j,\ldots}. \tag{2}$$

The partial molar volume can be thought of as the incremental volume obtained by adding a small amount of component i to an infinite sample of the mixture. The partial molar volume is not necessarily the same as the molar volume of the pure component as it depends on how the molecules interact and structure rearrange in the mixture. ($V_{m,i}$) can be calculated by equation (3) [53]:

$$V_{m,i} = V_m^{mix} + (1 - x_i)\frac{dV_m^{mix}}{dx_i}. \tag{3}$$

3. Results and discussion

(Liquid + liquid) equilibrium data obtained in this work are summarised in table 2 and shown in figure 1. In agreement with previously reported data [23–27], the solubility of water is found to be higher in $[C_1C_4Im][PF_6]$ than in $[C_1C_4Im][NTf_2]$. Furthermore, increasing in the alkyl chain length on the imidazolium ring, comparing $[C_1C_2Im][NTf_2]$ and $[C_1C_4Im][NTf_2]$, increases the hydrophobicity of the IL thus decreasing the solubility of water, as expected. For example, at 290 K the mole fraction of water is close to 0.285 and to 0.244 in $[C_1C_2Im][NTf_2]$ and $[C_1C_4Im][NTf_2]$, respectively. Moreover, for $[NTf_2]^-$-based ILs, the presence of a cyclic cation,

TABLE 2
Mole fraction solubilities of water (x_w) in hydrophobic ILs as a function of temperature.

T/K	x_w	T/K	x_w	T/K	x_w	T/K	x_w	T/K	x_w
[C$_1$C$_2$Im][NTf$_2$]		*[C$_1$C$_4$Im][NTf$_2$]*		*[C$_1$C$_4$Pyrro][NTf$_2$]*		*[N$_{4111}$][NTf$_2$]*		*[C$_1$C$_4$Im][PF$_6$]*	
285.15	0.2750	290.13	0.2431	278.46	0.1800	289.15	0.2043	295.76	0.2832
292.62	0.2970	299.32	0.2618	290.35	0.2260	298.15	0.2322	298.15	0.2970
298.25	0.3031	307.12	0.2891	297.17	0.2430	313.78	0.2564	303.27	0.3135
299.76	0.3040	319.76	0.3201	303.45	0.2650	323.45	0.2907	309.97	0.3401
303.22	0.3137	332.89	0.3571	308.01	0.2765	339.75	0.3192	318.62	0.3897
303.69	0.3214	345.19	0.3971	312.37	0.2921	345.82	0.3364	324.82	0.4231
315.62	0.3572	350.14	0.4123	319.21	0.3050	358.34	0.3876	333.76	0.4765
323.17	0.3921	360.05	0.4465	327.37	0.3250	362.62	0.4108	340.76	0.5084
329.44	0.4060	357.32	0.9983	333.21	0.3450	353.15	0.9996	347.00	0.5597
332.75	0.4150	345.83	0.9989	338.25	0.3685	332.15	0.9997	356.41	0.6563
338.38	0.4380	320.64	0.9994	345.11	0.3902	318.15	0.9998	354.97	0.9954
345.75	0.4855	310.38	0.9996	350.14	0.3996	298.15	0.9999	343.75	0.9966
353.18	0.5160	290.27	0.9998	357.17	0.4270			324.72	0.9974
358.09	0.5245			365.12	0.4390			314.24	0.9979
361.17	0.5330			358.06	0.9994			303.76	0.9982
345.11	0.9980			338.19	0.9995			298.15	0.9984
325.22	0.9985			318.24	0.9997				
302.43	0.9991			290.11	0.9998				
298.15	0.9992								
292.64	0.9995								

for example comparing [C$_1$C$_4$Im][NTf$_2$], [C$_1$C$_4$Pyrro][NTf$_2$] and [N$_{4111}$][NTf$_2$], increases the miscibility gap. For example, at 290 K the mole fraction of water is approximately 0.244, 0.225, and 0.206 in [C$_1$C$_4$Im][NTf$_2$], [C$_1$C$_4$Pyrro][NTf$_2$], and [N$_{4111}$][NTf$_2$], respectively.

Figure 2 shows the comparison of our data with literature for the system {[C$_1$C$_4$Im][PF$_6$] + water}. Although this graph shows differences between datasets, in general good agreement (typically less than 5% between our data and literature data) was obtained [21,24–27]. A limited number of studies have been reported with which to compare the other {IL + water} mixtures reported, herein. To date, only Freire *et al.* [21,22] have studied the liquid-liquid equilibrium of {water + [C$_1$C$_2$Im][NTf$_2$] or [C$_1$C$_4$Im][NTf$_2$] or [C$_1$C$_4$Pyrro][NTf$_2$]}, as a function of temperature. Good agreement was obtained over the temperature range (288.15 to 318.15) K. For example, the water mole fraction in the [C$_1$C$_2$Im][NTf$_2$] reported in this work and calculated by Freire *et al.* [22] are 0.3031 and 0.3003 at 298.25 K, respectively. The absolute average deviation between the data reported by Freire *et al.* [21,22] and those presented herein are 0.8% and 7% for the (liquid + liquid) equilibrium of {water + [C$_1$C$_4$Im][NTf$_2$]} and {water + [C$_1$C$_4$Pyrro][NTf$_2$]}, respectively.

Table 3 summarises the results for the density as a function of temperature between (293 and 343) K, for the pure ILs and for the mixtures {IL + water}. In table 4 the excess molar volumes for all the ILs studied, as a function of composition and temperature, calculated using equation (1) are shown. The excess molar volumes were correlated, at each temperature, as a function of composition by a Redlich–Kister-type equation:

$$V_m^E = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2]. \tag{4}$$

The coefficients A, B, and C are presented in table 5. Figure 3 presents the variation of the excess molar volumes as a function of the composition at 298 K.

Small excess volumes (less than 0.5 cm^3 · mol^{-1} at 298 K) are obtained compared with the molar volumes of the pure components (less than 0.3% of the molar volume of the pure IL). For all the systems studied, with the exception of [C$_1$C$_2$Im][EtSO$_4$], positive excess molar volumes were calculated. Negative deviations from ideality due to the presence of the ethylsulfate anion have

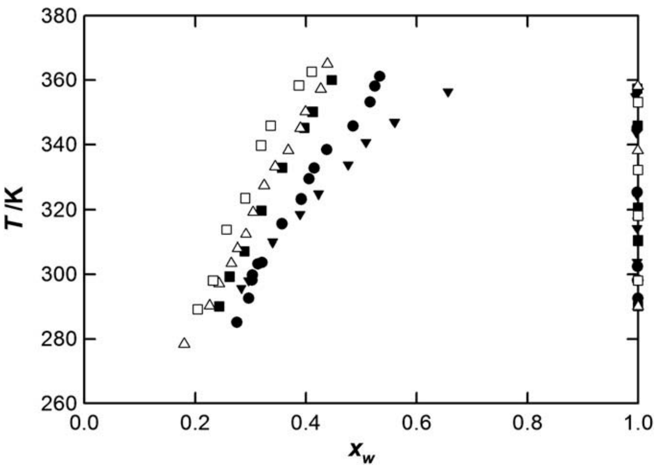

FIGURE 1. Liquid-liquid equilibrium data for the systems {water + hydrophobic IL}: •, [C$_1$C$_2$Im][NTf$_2$]; ■, [C$_1$C$_4$Im][NTf$_2$]; △, [C$_1$C$_4$Pyrro][NTf$_2$]; □, [N$_{4111}$][NTf$_2$]; ▼, [C$_1$C$_4$Im][PF$_6$].

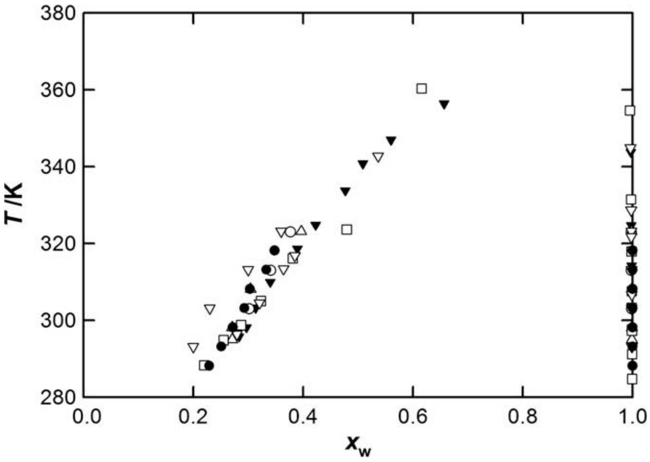

FIGURE 2. (Liquid + liquid) equilibrium data for the system {water + [C$_1$C$_4$Im][PF$_6$]}, comparison with literature data: ▼, our data; •, Freire *et al.* [21]; ○, Wong *et al.* [24]; △, Anthony *et al.* [25]; □, Najdanovic-Visak *et al.* [26]; ▽, Bendová *et al.* [27].

TABLE 3

Densities (ρ/g · cm^{-3}) of the seven {ILs + water} binary mixtures, ρ, as a function of the composition, expressed as the mole fraction of water, x_w, at temperatures between (293 and 343) K.

x_w	T/K										
	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
						[C_1C_2Im][$EtSO_4$]					
0	1.2424	1.2394	1.2363	1.2333	1.2302	1.2272	1.2241	1.2211	1.2181	1.2151	1.2120
0.0514	1.2414	1.2383	1.2352	1.2322	1.2291	1.2261	1.2230	1.2200	1.2169	1.2138	1.2107
0.1300	1.2398	1.2368	1.2336	1.2306	1.2274	1.2244	1.2213	1.2182	1.2152	1.2121	1.2089
0.1783	1.2388	1.2357	1.2326	1.2295	1.2263	1.2233	1.2201	1.2169	1.2139	1.2109	1.2078
0.2168	1.2378	1.2347	1.2315	1.2285	1.2254	1.2223	1.2191	1.2160	1.2129	1.2099	1.2067
0.2642	1.2364	1.2333	1.2302	1.2271	1.2239	1.2208	1.2176	1.2146	1.2115	1.2084	1.2053
0.3054	1.2350	1.2320	1.2288	1.2258	1.2226	1.2195	1.2163	1.2132	1.2101	1.2070	1.2039
0.3568	1.2330	1.2300	1.2269	1.2239	1.2207	1.2176	1.2144	1.2112	1.2082	1.2051	1.2019
0.4008	1.2312	1.2280	1.2250	1.2219	1.2187	1.2156	1.2124	1.2093	1.2062	1.2031	1.2000
0.4613	1.2281	1.2252	1.2220	1.2189	1.2156	1.2124	1.2093	1.2061	1.2031	1.2000	1.1968
0.5002	1.2259	1.2229	1.2197	1.2166	1.2134	1.2101	1.2069	1.2038	1.2007	1.1976	1.1943
0.5584	1.2218	1.2188	1.2156	1.2124	1.2092	1.2060	1.2028	1.1996	1.1964	1.1932	1.1899
0.6124	1.2171	1.2139	1.2108	1.2076	1.2044	1.2011	1.1978	1.1946	1.1914	1.1881	1.1847
0.6698	1.2107	1.2074	1.2041	1.2009	1.1976	1.1943	1.1910	1.1877	1.1843	1.1809	1.1774
0.7125	1.2043	1.2008	1.1976	1.1943	1.1909	1.1876	1.1843	1.1810	1.1775	1.1739	1.1704
0.7635	1.1942	1.1904	1.1871	1.1840	1.1806	1.1772	1.1737	1.1702	1.1668	1.1635	1.1599
0.8006	1.1842	1.1805	1.1772	1.1736	1.1703	1.1670	1.1635	1.1600	1.1566	1.1532	1.1495
0.8497	1.1654	1.1621	1.1588	1.1555	1.1523	1.1489	1.1452	1.1416	1.1383	1.1349	1.1313
0.8963	1.1393	1.1356	1.1328	1.1290	1.1260	1.1230	1.1196	1.1164	1.1129	1.1093	1.1060
1	0.9982	0.9970	0.9956	0.9940	0.9922	0.9901	0.9880	0.9857	0.9832	0.9805	0.9778

x_w	T/K		
	298.15	303.15	333.15
	[C_1C_4Im][BF_4]		
0	1.2011	1.1974	1.1754
0.0895	1.1983	1.1946	1.1728
0.1950	1.1944	1.1909	1.1690
0.3080	1.1893	1.1858	1.1639
0.4996	1.1778	1.1739	1.1515
0.7500	1.1479	1.1438	1.1210
0.8990	1.1007	1.0972	1.0764

x_w	T/K										
	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
						[N_{4111}][NTf_2]					
0	1.3995	1.3950	1.3905	1.3861	1.3816	1.3771	1.3726	1.3682	1.3637	1.3592	1.3548
0.0387	1.3984	1.3939	1.3894	1.3849	1.3805	1.3760	1.3715	1.3670	1.3624	1.3579	1.3534
0.0765	1.3970	1.3925	1.3880	1.3835	1.3790	1.3746	1.3700	1.3655	1.3609	1.3563	1.3518
0.1132	1.3953	1.3908	1.3863	1.3819	1.3774	1.3729	1.3684	1.3639	1.3593	1.3547	1.3502
0.1400	1.3941	1.3895	1.3850	1.3806	1.3761	1.3716	1.3671	1.3626	1.3580	1.3533	1.3487
0.1890	1.3924	1.3878	1.3832	1.3787	1.3741	1.3696	1.3651	1.3605	1.3558	1.3511	1.3464
0.2108	1.3918	1.3872	1.3825	1.3778	1.3732	1.3687	1.3641	1.3595	1.3548	1.3500	1.3451
0.2322	1.3912	1.3866	1.3818	1.3771	1.3724	1.3678	1.3632	1.3585	1.3537	1.3487	1.3438

x_w	T/K	x_w	T/K	x_w	T/K	x_w	T/K
	298.19		323.17		298.20		323.21
	[C_1C_2Im][NTf_2]				*[C_1C_4Im][NTf_2]*		
0	1.5193	0	1.4947	0	1.4371	0	1.4138
0.0209	1.5183	0.0353	1.4931	0.0308	1.4357	0.0482	1.4118
0.0499	1.5169	0.0581	1.4920	0.0753	1.4340	0.0816	1.4105
0.0631	1.5162	0.0834	1.4906	0.1194	1.4322	0.1190	1.4088
0.1205	1.5130	0.1164	1.4887	0.1731	1.4300	0.1597	1.4071
0.1608	1.5107	0.1611	1.4862	0.2391	1.4267	0.2141	1.4045
0.2032	1.5081	0.2221	1.4824			0.2583	1.4020
0.3025	1.5013						

x_w	T/K	x_w	T/K	x_w	T/K	x_w	T/K
	298.21		323.21		298.15		323.15
	[C_1C_4Pyrro][NTf_2]				*[C_1C_4Im][PF_6]*		
0	1.3953	0	1.3736	0	1.3683	0	1.3477
0.0435	1.3940	0.0298	1.3725	0.0431	1.3665	0.0431	1.3456
0.0654	1.3932	0.0673	1.3711	0.0982	1.3635	0.0982	1.3422
0.0860	1.3923	0.1012	1.3699	0.1222	1.3621	0.1222	1.3406
0.0913	1.3921	0.1406	1.3683	0.1566	1.3601	0.1566	1.3385
0.1262	1.3907	0.2033	1.3653	0.1873	1.3585	0.1873	1.3364
0.1396	1.3901			0.2548	1.3555	0.2548	1.3323
0.1909	1.3881			0.2971	1.3541	0.2971	1.3299
0.2228	1.3871						

TABLE 4
Excess molar volumes of the seven {ILs + water} binary mixtures, $V_m^E/(cm^3 \cdot mol^{-1})$, as a function of the composition, expressed as the mole fraction of water, x_w, at temperatures between (293 and 343) K.

x_w	T/K										
	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
						$[C_1C_2Im][EtSO_4]$					
0	0	0	0	0	0	0	0	0	0	0	0
0.0514	−0.036	−0.020	−0.019	−0.018	−0.017	−0.016	−0.015	−0.015	0.001	0.016	0.016
0.1300	−0.110	−0.107	−0.090	−0.087	−0.071	−0.070	−0.068	−0.053	−0.052	−0.038	−0.023
0.1783	−0.171	−0.153	−0.149	−0.132	−0.116	−0.114	−0.098	−0.070	−0.069	−0.069	−0.068
0.2168	−0.204	−0.186	−0.168	−0.164	−0.160	−0.145	−0.129	−0.115	−0.101	−0.101	−0.087
0.2642	−0.239	−0.221	−0.214	−0.197	−0.181	−0.166	−0.150	−0.148	−0.135	−0.122	−0.121
0.3054	−0.265	−0.257	−0.238	−0.232	−0.216	−0.201	−0.185	−0.171	−0.158	−0.147	−0.146
0.3568	−0.294	−0.284	−0.275	−0.268	−0.251	−0.237	−0.221	−0.197	−0.195	−0.184	−0.172
0.4008	−0.332	−0.302	−0.302	−0.284	−0.266	−0.252	−0.236	−0.223	−0.211	−0.200	−0.199
0.4613	−0.365	−0.362	−0.342	−0.323	−0.297	−0.273	−0.267	−0.244	−0.242	−0.232	−0.221
0.5002	−0.397	−0.384	−0.363	−0.344	−0.326	−0.295	−0.279	−0.266	−0.255	−0.246	−0.226
0.5584	−0.428	−0.413	−0.391	−0.365	−0.346	−0.324	−0.309	−0.288	−0.270	−0.253	−0.235
0.6124	−0.455	−0.425	−0.409	−0.383	−0.364	−0.336	−0.313	−0.293	−0.276	−0.253	−0.229
0.6698	−0.477	−0.441	−0.411	−0.385	−0.359	−0.332	−0.310	−0.285	−0.256	−0.229	−0.200
0.7125	−0.471	−0.423	−0.399	−0.367	−0.336	−0.310	−0.288	−0.264	−0.231	−0.195	−0.168
0.7635	−0.446	−0.385	−0.355	−0.334	−0.304	−0.274	−0.242	−0.209	−0.184	−0.167	−0.137
0.8006	−0.406	−0.352	−0.321	−0.277	−0.252	−0.228	−0.197	−0.166	−0.142	−0.122	−0.090
0.8497	−0.311	−0.275	−0.244	−0.213	−0.192	−0.165	−0.128	−0.095	−0.077	−0.058	−0.034
0.8963	−0.219	−0.170	−0.153	−0.107	−0.091	−0.077	−0.053	−0.036	−0.012	0.011	0.024
1	0	0	0	0	0	0	0	0	0	0	0

x_w	T/K		
	298.15	303.15	333.15
	$[C_1C_4Im][BF_4]$		
0	0	0	0
0.0895	0.129	0.133	0.123
0.1950	0.267	0.251	0.280
0.3080	0.392	0.384	0.439
0.4996	0.477	0.519	0.659
0.7500	0.399	0.454	0.644
0.8990	0.203	0.236	0.360
1	0	0	0

x_w	T/K										
	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
						$[N_{4111}][NTf_2]$					
0	0	0	0	0	0	0	0	0	0	0	0
0.0387	0.014	0.016	0.018	0.040	0.022	0.024	0.025	0.047	0.069	0.071	0.093
0.0765	0.074	0.078	0.083	0.106	0.110	0.094	0.117	0.140	0.163	0.186	0.210
0.1132	0.175	0.182	0.189	0.195	0.201	0.207	0.212	0.236	0.260	0.285	0.309
0.1400	0.204	0.231	0.240	0.247	0.255	0.262	0.269	0.294	0.319	0.363	0.406
0.1890	0.206	0.234	0.262	0.289	0.316	0.325	0.335	0.378	0.422	0.465	0.527
0.2108	0.161	0.189	0.234	0.295	0.323	0.333	0.360	0.404	0.448	0.508	0.605
0.2322	0.114	0.143	0.204	0.264	0.309	0.336	0.364	0.424	0.484	0.578	0.674

x_w	T/K	x_w	T/K	x_w	T/K	x_w	T/K
	298.19		323.17		298.20		323.21
	$[C_1C_2Im][NTf_2]$				$[C_1C_4Im][NTf_2]$		
0	0	0	0	0	0	0	0
0.0209	0.033	0.0353	0.057	0.0308	0.103	0.0482	0.141
0.0499	0.076	0.0581	0.098	0.0753	0.170	0.0816	0.196
0.0631	0.095	0.0834	0.145	0.1194	0.223	0.1190	0.283
0.1205	0.193	0.1164	0.221	0.1731	0.245	0.1597	0.325
0.1608	0.236	0.1611	0.278	0.2391	0.314	0.2141	0.389
0.2032	0.280	0.2221	0.349			0.2583	0.459
0.3025	0.313						

x_w	T/K	x_w	T/K	x_w	T/K	x_w	T/K
	298.21		323.21		298.15		323.15
	$[C_1C_4Pyrro][NTf_2]$				$[C_1C_4Im][PF_6]$		
0	0	0	0	0	0	0	0
0.0435	0.058	0.0298	0.090	0.0431	0.051	0.0431	0.106
0.0654	0.100	0.0673	0.172	0.0982	0.182	0.0982	0.307
0.0860	0.148	0.1012	0.241	0.1222	0.238	0.1222	0.394
0.0913	0.169	0.1406	0.320	0.1566	0.301	0.1566	0.475
0.1262	0.224	0.2033	0.467	0.1873	0.317	0.1873	0.559
0.1396	0.255			0.2548	0.244	0.2548	0.616
0.1909	0.304			0.2971	0.115	0.2971	0.591
0.2228	0.265						

also been reported in literature [34,39]. For the two highest temperatures studied for water-rich mixtures, slightly positive excess molar volumes are measured. This behaviour has also been already observed in literature [34,39]. This may be due to the dissociation of the ion pairs forming the ILs due to the strong hydrogen bonding accepting ability of the anion [39].

For all the other ILs, no significant differences are observed in the excess molar volumes. In particular, no effect of the anion is discernable. For all the systems presenting positive excess molar volumes, similar increases in the excess volume with composition are observed until a maximum is reached for a mole fraction of water around 0.2 for the five systems containing hydrophobic ILs and for equimolar composition ($x_w = 0.55$) in the case of $[C_1C_4Im][BF_4]$. For $[N_{4111}][NTf_2]$, $[C_1C_4pyrro][NTf_2]$, and $[C_1C_4Im][PF_6]$, the decrease of the excess molar volume and the fact that excess molar volume is equal to zero for pure components, indicates that we would observe an S-shape if the two components were fully miscible. An increase of the non-ideality of all the systems is observed as temperature increases.

The volumetric properties of mixtures composed of water and of an IL fully miscible with water have been studied by a number of researchers. This data has been compared with the results presented, herein, to estimate the accuracy of the data in the present work. The experimental excess molar volumes from various literature sources and from this work are presented in figures 4 and 5 for the systems $\{[C_1C_4Im][BF_4]$ and $[C_1C_2Im][EtSO_4] + \text{water}\}$, respectively.

For $\{[C_1C_4Im][BF_4] + \text{water}\}$, the values of Rebelo *et al.* [29] deviate from our experimental data by less than 5% (average deviation 1.5%). The excess molar volumes measured by Malham *et al.* [28] are systematically lower than the data measured in the present work (deviations lower than 10% at water mole fraction higher than 0.5 and deviations between 20% and 40% for the water mole fractions lower than 0.5). The experimental data of Liu *et al.* [54] is not coherent with the previous series of data. Therein, negative excess molar volumes for water mole fraction between 0.4 and 0.6 were observed. In addition, the work of Zhang *et al.* [55] with excess molar volumes between (3 and 8) $cm^3 \cdot mol^{-1}$ was not considered in this comparison.

For $\{[C_1C_2Im][EtSO_4] + \text{water}\}$, the values of Rodriguez and Brennecke [34] deviate from our experimental data by less than 5%, except at the extreme mole fractions of water or IL where the excess molar volumes are close to zero. Our data are systematically lower than those presented by Gomez *et al.* [39] (average deviation 25%) and higher than those presented by Lu *et al.* [56] and Yang *et al.* [57] (average deviation 45%). Finally the experimental excess

TABLE 5
Parameters *A*, *B*, and *C* of the Redlich–Kister-type fittings, equation (4), used to fit the experimental excess molar volumes from table 4 as a function of the composition and temperature along with the per cent average absolute deviation of the fit (AAD).

T/K	$A/(cm^3 \cdot mol^{-1})$	$B/(cm^3 \cdot mol^{-1})$	$C/(cm^3 \cdot mol^{-1})$	AAD/%
		$[C_1C_2Im][EtSO_4]$		
293.15	−1.6273	1.1434	−0.4322	5.6
298.15	−1.5611	0.9580	−0.0297	8.3
303.15	−1.4966	0.8653	0.1390	7.3
308.15	−1.4249	0.7252	0.3417	2.3
313.15	−1.3438	0.6625	0.4541	7.4
318.15	−1.2458	0.5717	0.4705	2.1
323.15	−1.1873	0.4822	0.6854	2.4
328.15	−1.1176	0.4133	0.8835	4.8
333.15	−1.0667	0.3164	1.0496	2.6
338.15	−1.0094	0.2259	1.1838	9.4
343.15	−0.9511	0.1070	1.3130	4.9
		$[C_1C_4Im][BF_4]$		
298.15	1.9342	−0.3628	0.0108	1.3
303.15	2.0681	−0.6932	0.0145	1.8
333.15	2.6302	−1.5225	0.1844	0.3
		$[N_{4111}][NTf_2]$		
293.15	−14.419	−44.537	−30.826	7.1
298.15	−15.233	−47.703	−33.331	5.9
303.15	−12.615	−41.375	−29.440	4.1
308.15	−7.8468	−28.326	−20.320	2.8
313.15	−7.7289	−29.251	−21.667	6.8
318.15	−7.2691	−28.603	−21.622	4.7
323.15	−5.2339	−22.927	−17.528	8.4
328.15	−2.5976	−15.915	−12.446	3.8
333.15	0.0704	−8.8128	−7.2965	2.1
338.15	2.7062	−2.7087	−3.4002	4.9
343.15	5.6788	4.0979	0.9630	2.2
		$[C_1C_2Im][NTf_2]$		
298.19	0.2396	−4.3872	−3.1484	1.9
323.17	−0.8836	−8.8677	−6.5736	1.8
		$[C_1C_4Im][NTf_2]$		
298.20	0.5836	−2.0313		8.4
323.21	4.1893	6.5499	5.8148	2.1
		$[C_1C_4pyrro][NTf_2]$		
298.21	−8.7972	−30.345	−21.059	2.1
323.21	3.2887	0.7503		4.6
		$[C_1C_4Im][PF_6]$		
298.15	−7.0426	−26.107	−18.385	4.5
323.15	−1.9591	−16.918	−12.720	2.9

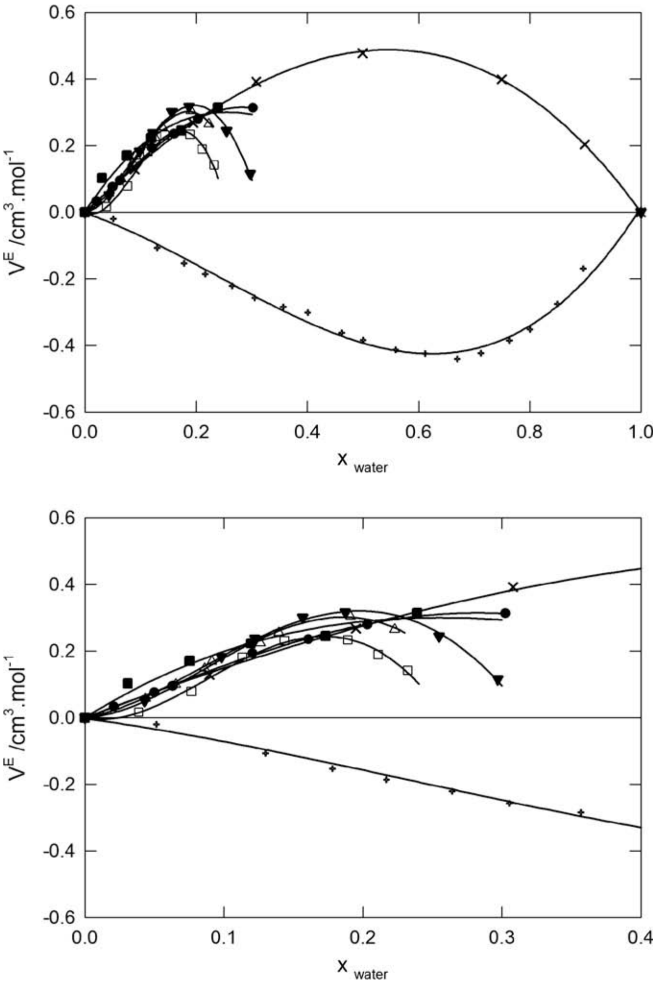

FIGURE 3. Excess molar volumes of the {IL + water} binary mixtures as a function of the water mole fraction, x_w, at 298 K: +, $[C_1C_2Im][EtSO_4]$; ×, $[C_1C_4Im][BF_4]$; ▼, $[C_1C_4Im][PF_6]$; ■, $[C_1C_4Im][NTf_2]$; •, $[C_1C_2Im][NTf_2]$; □, $[N_{4111}][NTf_2]$; △, $[C_1C_4Pyrro][NTf_2]$. The lines represent the Redlich–Kister type fittings with the parameters indicated in table 5.

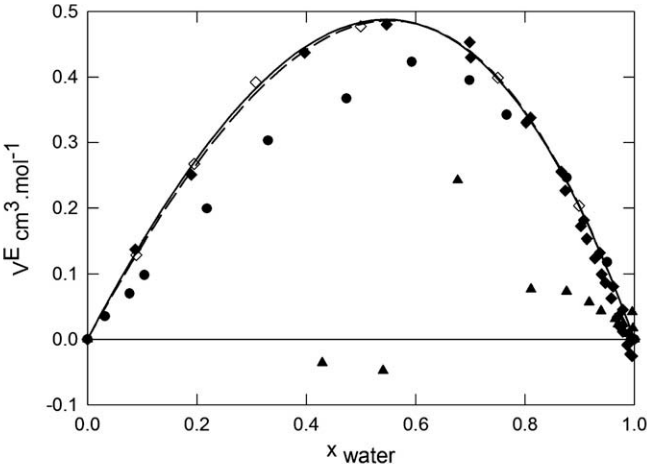

FIGURE 4. Excess molar volumes of the {water + [C_1C_4Im][BF_4]} binary mixture as a function of the water mole fraction at 298 K: (●), Malham *et al.* [28]; (⧫), Rebelo *et al.* [29]; (▲), Liu *et al.* [54]; (◇), this work. Lines correspond to the fit of the experimental data, (—), this work; (— —), Rebelo *et al.* [29].

molar volumes measured by Vila *et al.* [58] are not coherent with the previous sets of data (positive values). These relatively high deviations are likely to be due to errors in the composition of the mixtures studied as the two components have very different volatilities.

In figure 6 are presented the partial molar volumes of water in the different ILs at $x_w = 0.2$ and $T = 298$ K, calculated using equation (3). They can be compared with the molar volume of pure water at the same temperature (18.064 cm^3 · mol^{-1}) [59]. The partial molar volume of water in the two hydrophilic ILs, [C_1C_2Im][C_2SO_4] and [C_1C_4Im][BF_4], is very different. In the first case, it is lower than the molar volume of pure water and in the second it is significantly higher. This behaviour is in direct relation with the excess volumes determined for these two ILs which are completely miscible with water: {[C_1C_2Im][$EtSO_4$] + water} and {[C_1C_4Im][BF_4] + water} have negative and positive excess volumes, respectively. Just by analysing their volumetric behaviour no conclusions can be drawn on the molecular interactions involved in these mixtures. In fact, the partial molar volume of water is proportional to the variation of its activity coefficient with pressure [60] and enthalpic information is necessary to provide information about the behaviour with temperature of the Gibbs free energy and so have the necessary information to fully interpret the behaviour of these mixtures at a molecular level. As the molar volume of the ILs studied is much larger than that of water, the variations of their partial molar volumes in the mixtures are much less perceptible.

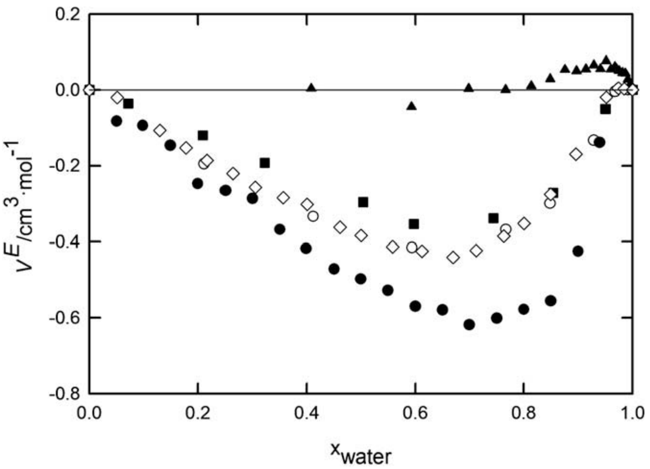

FIGURE 5. Excess molar volumes of the {water + [C_1C_2Im][$EtSO_4$]} binary mixture as a function of the water mole fraction at 298 K: (▲), Vila *et al.* [58]; (●), Lu *et al.* [56], Yang *et al.* [57]; (■), Gomez *et al.* [39]; (○), Rodriguez and Brennecke [34]; (◇), this work.

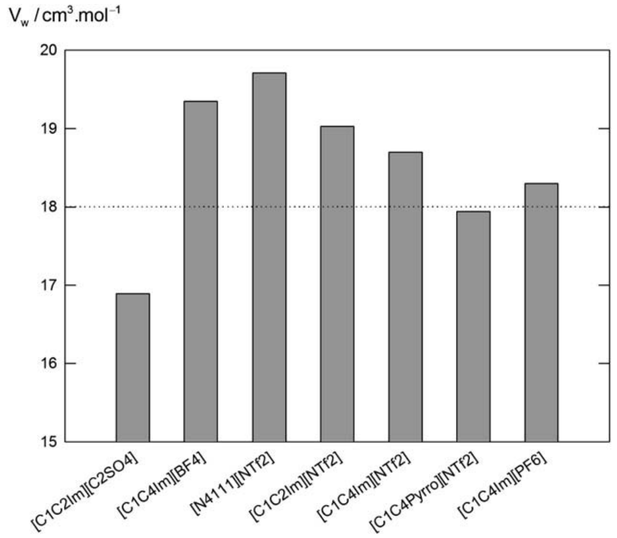

FIGURE 6. Partial molar volumes of water in ILs at 298 K ($x_w = 0.2$). The dotted line corresponds to the molar volume of pure water.

For the hydrophobic ILs, the partial molar volume of water is similar in all the mixtures studied, showing the highest value in the mixture with [N_{4111}][NTf_2] and the lowest value with [C_1C_4Pyrro][NTf_2]. This behaviour for the partial molar volume of water is compatible with the positive excess volumes measured for the mixtures at this temperature and composition. The more positive excess molar volumes values do not correspond to the larger partial molar volumes of water, as [C_1C_4Im][PF_6] has the larger positive value for the excess volume and not water does not have the larger partial molar volume in this mixture.

4. Conclusions

The phase behaviour and volumetric properties of several {water + IL} binary mixtures were studied as a function of temperature from (288 to 318) K. For the two ILs fully miscible with water, a comparison with literature was possible. The study of the volumetric properties of aqueous mixtures containing a hydrophobic IL constitutes an original work. For all the systems, small excess molar volumes (less than 0.5 cm^3 · mol^{-1} at 298 K) are obtained compared to the molar volumes of the pure components (less than 0.3% of the molar volume of the pure IL). For all the systems studied, with the exception of [C_1C_2Im][$EtSO_4$], positive excess molar volumes were calculated. No significant effect on the volumetric properties was observed when changing the anion or the cation of the IL. Finally, an increase of the non-ideality is observed for all the systems as temperature increases.

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