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Deviations from Ideality in Mixtures of Two Ionic Liquids Containing a Common Ion

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Excess molar volumes of six binary mixtures composed of two ionic liquids of the 1-methyl-3-alkyl-imidazolium bis(trifluoromethylsulfonyl)amide family— $[\text{C}_m\text{mim}] + [\text{C}_n\text{mim}][\text{NTf}_2]$ with n and m ranging from 2 to 10—were measured for several compositions at 298 and 333 K. Similarly, three other binary systems containing $[\text{C}_4\text{mim}]^+$ (1-methyl-3-butylimidazolium) as a common cation have been studied: $[\text{C}_4\text{mim}][\text{NTf}_2] + [\text{PF}_6]$, $[\text{C}_4\text{mim}][\text{NTf}_2] + [\text{BF}_4]$ and $[\text{C}_4\text{mim}][\text{BF}_4] + [\text{PF}_6]$. Thus, the mixing process of two distinct ions of equal sign embedded in a constant field network of a given counterion was analyzed. All systems exhibit small, positive V^E values of the order of a few tenths of $\text{cm}^3 \text{mol}^{-1}$, which are essentially temperature and pressure independent. The results show additive trends, for instance, the V^E values become larger as the difference between the alkyl chain lengths of the two cations increases. The Flory theory of mixtures provides a useful, semiquantitative correlation between the excess volumes and excess enthalpies in these systems, allowing for comparison with analogous results obtained within the linear primary alcohols.

1. Introduction

In recent years, the properties of room-temperature ionic liquids, or simply ionic liquids (ILs), have attracted considerable attention.^{1,2} They are normally low-melting organic salts, solely composed of anions and cations (making them markedly different from ionic solutions, which contain ions dissolved in a molecular medium) and, generally, are liquid at around (and often below) room temperature. Their perceived status as “designer”, alternative “green” solvents has contributed largely to this interest, namely the existence of fluids with no measurable volatility that are able to selectively dissolve different types of solute merely by exchanging one of the ions that form the IL or, even more subtly, by altering one of the organic residues within a given ion. In other words, their properties, and, thus, their behavior with respect to their solvating ability, can usually be “coarse-tuned” either by changing the chemical nature of the cation or that of the anion. The “fine-tuning” of their characteristics is usually achieved by slightly changing the cation's size, typically by altering the alkyl chain length of its organic residue, while preserving its chemical nature. There already are a considerable number of known pure ionic liquids, with an estimated minimum of a million being available.^{2g}

In addition, the number of available ILs can be easily and significantly increased by considering their binary (yielding over 10^{12} combinations) or ternary mixtures (yielding over 10^{18} combinations). The properties of these mixtures should be easily predictable once information regarding their pure components is available. A priori and at a first level of approximation, one

should expect the mixtures' properties to be merely the weighted (by the mole fraction) mean value of those of the pure ILs (quasi-ideal mixture). Torres³ tackled, for the first time, the search for excess effects upon the homogeneous mixture of two ILs. In respect to the volumetric properties, her results accurately reveal that, in practice, these homogeneous binary mixtures can be considered ideal but her data are inconclusive regarding the value and sign of the small excess effect due to the relatively low precision achieved.

Although the characterization of ILs as solvents, or reaction media, has been established for a large number of systems, the thermophysical description and/or molecular modeling of ILs is by no means so extensive; even less is known about their mixtures. In this work, we investigate the truism of the assumption of ideality for IL mixtures, keeping in mind that there is already experimental evidence⁴ that some binary mixtures of ILs are heterogeneous (liquid–liquid phase separation), and, therefore, in this sense, highly nonideal.

The primary objective of this work is to provide some quantitative insight concerning the experimental volumetric behavior of ionic liquid mixtures. The second aim is to discuss their enthalpic behavior theoretically, and the final aim is to explore ways to establish predictive tools for estimating deviations from ideality in these mixtures. We focus our attention on the observation that, although electrostatic forces play a predominant role in the intermolecular forces acting in ILs (their extremely low volatility is one of the most obvious consequences of this fact), in many cases ILs appear to act in a manner similar to weakly polar, aprotic organic solvents, although this is by no means always the case.⁵ The apparent lack of effect of their ionic character when interacting with a weakly polarized solute, and the importance of the organic residues of a given ion in those same interactions, is another way to formulate the same observation.

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The binary IL mixtures investigated in the present study always consist of two different ionic liquids with either a common cation or a common anion. This means that the mixtures are conceptually very simple (the complexity associated with the inclusion of either a non-IL component or two completely different ILs is removed), i.e., any changes in the volumetric behavior of the mixture can be related to changes in a single molecular entity.

2. Experimental Section

Chemicals. All ionic liquids used in this work, namely, 1-methyl-3-alkyl-imidazolium bis(trifluoromethylsulfonyl)-amides, $[C_n\text{mim}][\text{NTf}_2]$ (n ranging from 2 to 10), and 1-methyl-3-butyl-imidazolium hexafluorophosphate or tetrafluoroborate, $[C_4\text{mim}][\text{PF}_6]$ or $[C_4\text{mim}][\text{BF}_4]$, respectively, were synthesized at QUILL (The Queen's University Ionic Liquid Laboratories, Belfast), where they underwent first-stage purification. The exception was $[C_4\text{mim}][\text{BF}_4]$ which was supplied by Solvent Innovation. NMR analyses showed no major impurities in the untreated, original samples, except for the presence of water. All samples were further thoroughly degassed, dried, and freed from any small traces of volatile compounds by applying vacuum (0.1 Pa) at moderate temperatures (60–80 °C) for at least 24 h. Then, both the water and chloride contents were analyzed. Karl Fischer titrations revealed very low levels of water (below 70 ppm) for all treated ILs. The Cl^- specific electrode using the standard addition method has generally shown chloride contents in the range of 20–150 ppm.⁶

Equipment. Atmospheric pressure density measurements were performed in an Anton-Paar DMA 5000 vibrating-tube densimeter with temperature stability better than 0.005 K over periods of more than 10 min. Pressure-dependent density measurements were carried out in an Anton Paar DMA 512P densimeter, capable of reaching pressures up to 60 MPa, which was connected to a bath with a temperature stability of 0.01 K. Descriptions of the pressurizing apparatus and the calibration procedures can be found elsewhere.⁷ Typically, density precisions are 0.001% and 0.002%, respectively, while, owing to inconsistencies associated with the calibrating fluids' data and the samples' impurity, the corresponding overall accuracies are about one to 2 orders of magnitude lower.

Procedure. The composition of the mixtures was determined by a standard gravimetric method (balance), i.e., they were prepared by weighing the necessary amount of each component directly into a small (ca. 5 cm³), sealed glass vial to an estimated uncertainty of $\pm 0.02\%$ (mass percentage). The thorough mixing of the two components was promoted by the movement of a small glass sphere (inserted in the vial prior to the addition of the ILs) as the flask was slowly and repeatedly inverted. After mixing, the homogeneous liquid (ca. 3 cm³) was transferred to a syringe and injected into the densimeter. To check whether the mixture was well homogenized, the vibrating tube was first filled with some of the contents of the syringe (ca. 1 cm³), and a first density measurement was taken (after the temperature set point was reached). Another measurement followed when the contents of the vibrating tube were replaced with the mixture that remained in the syringe. The agreement between both values is a measure of the effectiveness of the mixing process. To guarantee the good internal consistency of the excess molar volume results, the densities of both pure components used to prepare a given binary mixture were also determined under experimental conditions similar to those employed during the density determination of the mixture (during the same series of

TABLE 1: Excess Molar Volumes of Binary Mixtures Containing Two ILs with a Common Anion ($[\text{NTf}_2]^-$)^a

x	V (pure component) or $V^E/\text{cm}^3\cdot\text{mol}^{-1}$	
	$T = 298.15 \text{ K}$	$T = 333.15 \text{ K}$
($[\text{C}_2\text{mim}] + [\text{C}_{10}\text{mim}][\text{NTf}_2]$)		
1	257.873 (257.9)	263.969 (264.0)
0.798	0.15 ₉	0.14 ₂
0.603	0.24 ₉	0.22 ₂
0.499	0.24 ₅	0.23 ₄
0.400	0.25 ₀	0.22 ₈
0.205	0.16 ₈	0.16 ₅
0	404.061 (404.0)	413.775 (413.5)
($[\text{C}_4\text{mim}] + [\text{C}_{10}\text{mim}][\text{NTf}_2]$)		
1	292.490 (292.4)	299.414 (299.3)
0.500	0.22 ₁	0.23 ₁
0.250	0.16 ₀	0.17 ₇
0	404.351 (404.0)	413.872 (413.5)
($[\text{C}_6\text{mim}] + [\text{C}_{10}\text{mim}][\text{NTf}_2]$)		
1	326.222 (326.2)	334.058 (334.1)
0.836	0.05 ₃	0.06 ₁
0.660	0.09 ₁	0.09 ₃
0.556	0.11 ₀	0.11 ₅
0.463	0.15 ₉	0.11 ₁
0.246	0.07 ₁	0.10 ₆
0	404.021 (404.0)	413.736 (413.5)
($[\text{C}_8\text{mim}] + [\text{C}_{10}\text{mim}][\text{NTf}_2]$)		
1	361.784 (361.8)	370.508 (370.5)
0.501	0.08 ₄	0.07 ₇
0	406.689 (404.0)	416.532 (413.5)
($[\text{C}_4\text{mim}] + [\text{C}_8\text{mim}][\text{NTf}_2]$)		
1	292.349 (292.4)	299.309 (299.3)
0.472	0.13 ₉	0.11 ₉
0.471	0.13 ₉	0.11 ₉
0	362.141 (361.8)	370.874 (370.5)
($[\text{C}_2\text{mim}] + [\text{C}_8\text{mim}][\text{NTf}_2]$)		
1	257.985 (257.9)	264.064 (264.0)
0.750	0.11 ₅	0.11 ₈
0.500	0.12 ₁	0.12 ₄
0.250	0.12 ₈	0.12 ₅
0	362.539 (361.8)	371.182 (370.5)

^a x defines the molar fraction of the first IL. "Reference" values for the molar volumes of pure ILs are given between parentheses, see text. Independent literature data can be found in ref 2.

density determinations, with all samples being prepared simultaneously from the same batch of pure components).

3. Results and Discussion

Tables 1 and 2 contain density data (translated as molar volumes) for the nine binary mixtures under discussion (the six mixtures with a common anion plus three with a common cation). The excess volume data were calculated taking into account the definition of an excess property, $V^E = V_{\text{mix}} - V_{\text{ideal}} = V_{\text{mix}} - x_1V_1 - x_2V_2$, where V_{mix} , V_{ideal} , V_1 , and V_2 are the molar volumes of the mixture, of the hypothetical ideal mixture, and of the two pure components, respectively, and x_i ($i = 1$ or 2) are the corresponding mole fractions. Also in the tables are the molar volume values of the pure ILs used to prepare each set of mixtures. Small fluctuations in these latter values reflect the fact that the ILs used in different sets of mixtures underwent different degrees of degassing and drying while different densimeters were also used. However, such scattering in the data does not affect the V^E results owing to the cancellation effect implicit in the definition of an excess property, provided an internally consistent procedure is followed (see above, under Experimental; Procedure). Reference values for the molar volume of each pure IL are also given between parentheses in

TABLE 2: Excess Molar Volumes of Binary Mixtures Containing Two ILs with a Common Cation ([C₄mim]⁺)^a

x	V (pure component) or V ^E /cm ³ ·mol ⁻¹	
	T = 298.15 K	T = 333.15 K
[C ₄ mim]([PF ₆] + [NTf ₂])		
1	207.811 (207.8)	212.291 (212.3)
0.750	0.09 ₅	0.07 ₆
0.500	0.12 ₀	0.10 ₇
0.250	0.13 ₁	0.10 ₉
0	292.453 (292.4)	299.375 (299.0)
[C ₄ mim]([PF ₆] + [BF ₄])		
1	207.986 (207.8)	212.470 (212.3)
0.600	0.13 ₉	0.13 ₇
0.500	0.11 ₈	0.11 ₀
0.400	0.13 ₃	0.12 ₈
0	187.634 (187.6)	191.558 (191.4)
1	207.826 (207.8)	212.308 (212.3)
0.500	0.12 ₅	0.11 ₆
0.250	0.09 ₂	0.09 ₀
0	187.634 (187.6)	191.558 (191.6)
[C ₄ mim]([BF ₄] + [NTf ₂]) ^b		
	T = 303.15 K	T = 333.15 K
1	188.042 (188.0)	191.367 (191.4)
0.977	0.10 ₂	0.10 ₁
0.899	0.14 ₇	0.21 ₈
0.699	0.27 ₅	0.28 ₀
0.450	0.28 ₇	0.25 ₇
0.301	0.28 ₉	0.25 ₀
0.102	0.14 ₀	0.11 ₈
0	292.794 (292.8)	299.005 (299.0)

^a x defines the molar fraction of the first IL. "Reference" values for the molar volumes of pure IL are given between parentheses, see text. Independent, literature data can be found in ref 2. ^b V^E values insensitive (within ± 0.01 cm³ mol⁻¹) to pressure up to 60 MPa.

Tables 1 and 2 and can be regarded as the values reflecting the degree of precision and accuracy one is expected to obtain while comparing the density of pure ILs from different sources. Judging from the repeatability of the results within each binary mixture including those presenting slightly different density values for a given pure IL component, the estimated uncertainty of the V^E results are typically ±0.02 cm³ mol⁻¹ and ±0.03 cm³ mol⁻¹, respectively, for the ambient pressure and the high pressure determinations.

Figure 1a and 1b depict, using two examples, the symmetrical behavior of the excess volumes versus composition for these systems. Irrespective of the nature of the mixture (common anion or common cation), all excess molar volumes are small (of the order of tenths of cm³ mol⁻¹—less than 0.1% of the mixture's molar volume) and positive. It was also found that the V^E values for these homogeneous [IL(1) + IL(2)] liquid mixtures are basically insensitive to temperature and (essentially) pressure changes within the working *p*, *T* ranges when compared with the claimed experimental uncertainties. The extreme showcase for this fact is provided by the constant values (within ± 0.01 cm³ mol⁻¹) of V^E for [C₄mim] ([NTf₂] + [BF₄]) along isotherms up to 60 MPa. This is to be expected owing to the predictably broad *p*, *T* liquidus range {since, although real or hypothetical liquid–gas critical points are unknown, they can be predicted to occur at extremely high (temperature, pressure) coordinates} and as a result changes of the order of tens of Kelvin and/or tens of MPa correspond to tiny shifts in terms of reduced *p*, *T* variables.

The results also revealed additive trends, i.e., the V^E values become larger as the difference between the sizes of the two cations or anions increases. In the [C₄mim] ([NTf₂] + [PF₆]), [C₄mim] ([NTf₂] + [BF₄]) and [C₄mim] ([BF₄] + [PF₆]) series, while the excess volume in the "([NTf₂]⁻ + [PF₆]⁻)" or in the

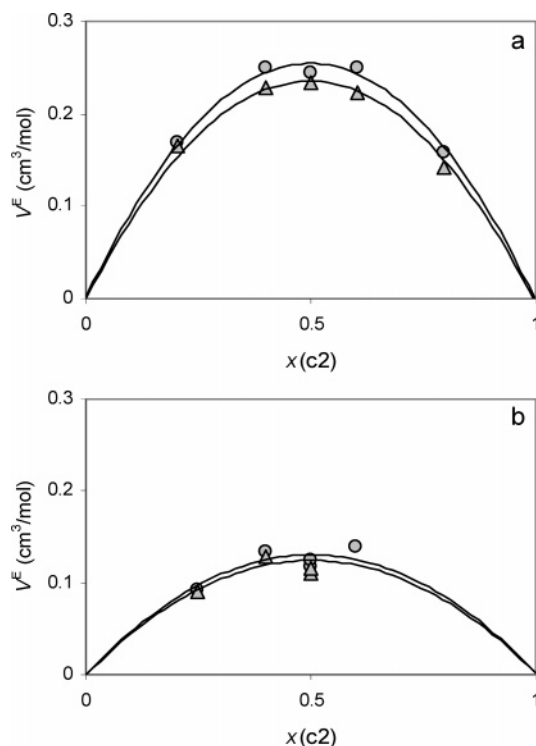


Figure 1. Excess molar volume as a function of composition in two selected IL binary mixtures: (a) ([C₂mim] + [C₁₀mim])[NTf₂]; (b) [C₄mim]([PF₆] + [BF₄]). (circles) 298.15 K; (triangles) 333.15 K.

"([BF₄]⁻ + [PF₆]⁻)" systems is around 0.12 cm³ mol⁻¹, the excess volume is approximately 0.28 cm³ mol⁻¹ in the "([NTf₂]⁻ + [BF₄]⁻)" system. This is consistent with the fact that, in terms of size, [NTf₂]⁻ > [PF₆]⁻ > [BF₄]⁻. The molar effective "sizes" of these anions⁸ are 158.7, 73.7, and 53.4 cm³ mol⁻¹, respectively.

Similar behavior is observed within the ([C_mmim] + [C_nmim]) [NTf₂] series, where the difference between the two ionic liquids lies only in the length of their cation's *N*-alkyl chains.

Comparison with Mixtures of Linear Alcohols. A more quantitative interpretation of the results can be conducted if one takes into account the volumetric behavior of alcohol mixtures. Binary mixtures of linear alcohols of different chain length, (C_mOH + C_nOH), constitute in our opinion a good analogy to the "([C_mmim]⁺ + [C_nmim]⁺)" mixtures, since, in both cases, we have an aliphatic chain of variable size attached by one of its ends to a group where strong intermolecular interactions occur (electrostatic and hydrogen bonding in the case of the imidazolium residue; hydrogen bonding in the hydroxyl group case).

The excess molar volumes of binary mixtures of linear alcohols (methanol to decanol) were measured more than thirty years ago.⁹ Likewise in the case of the IL mixtures under discussion, the alcohol mixtures V^E values are also positive and small (in the 0–0.2 cm³ mol⁻¹ range, i.e., less than 0.1% of the mixture's molar volume) and also show an additive trend. A comparison between the equimolar excess molar volumes in these two types of system is presented in Table 3 and in Figures 2 and 3. The analogy between the two systems is obvious in Figure 2 but even more striking in Figure 3, where the equimolar excess molar volumes are represented in a reduced form (V^{E*}_{1/2} = V^E_{1/2}/V_{ideal}).

In both representations, it is clear that, in mixtures where the methanol molecule is included, the excess molar volume

TABLE 3: Comparison between Experimental and Calculated Data Concerning IL and Alcohol Binary Mixtures with Components with Different Alkyl Chain Length^a

system	$V^E_{1/2}/\text{cm}^3\cdot\text{mol}^{-1}$	$H^E_{1/2}/\text{kJ}\cdot\text{mol}^{-1}$	$X_{12}/\text{J}\cdot\text{cm}^{-3}$	labels in Figures 6 and 8
Ionic Liquid Mixtures ($[\text{C}_m\text{mim}] + [\text{C}_n\text{mim}][\text{NTf}_2]$)				
	exp. ^{this work}	calc. ^{this work}	calc. ^{this work}	
$\text{C}_2 + \text{C}_8$	0.14	0.31	4.6	1
$\text{C}_2 + \text{C}_{10}$	0.25	0.56	8.2	2
$\text{C}_4 + \text{C}_8$	0.13	0.29	4.1	3
$\text{C}_4 + \text{C}_{10}$	0.22	0.50	7.1	4
$\text{C}_6 + \text{C}_{10}$	0.11	0.25	3.2	5
$\text{C}_8 + \text{C}_{10}$	0.08	0.18	2.2	6
Alcohol Mixtures ($\text{C}_m\text{OH} + \text{C}_n\text{OH}$)				
	calc. ⁹ (exp.) ⁹	exp. ⁹ (calc.) ^{this work}	calc. ⁹	
$\text{C}_1 + \text{C}_2$	0.007 (0.009)	0.005 (0.007)	0.6	
$\text{C}_1 + \text{C}_3$	0.065 (0.050)	0.083 (0.065)	8.6	
$\text{C}_1 + \text{C}_4$	0.091	0.145	14.3	
$\text{C}_1 + \text{C}_6$	0.132 (0.116)	0.245 (0.223)	22.7	
$\text{C}_1 + \text{C}_8$	0.167	0.353	31.1	
$\text{C}_1 + \text{C}_{10}$	0.142 (0.178)	0.418 (0.474)	35.6	
$\text{C}_2 + \text{C}_3$	0.010 (0.008)	0.020 (0.018)	1.6	
$\text{C}_2 + \text{C}_4$	0.014	0.049	3.7	
$\text{C}_2 + \text{C}_6$	0.040 (0.036)	0.128 (0.124)	9.0	
$\text{C}_2 + \text{C}_8$	0.066	0.223	14.6	1
$\text{C}_2 + \text{C}_{10}$	0.057 (0.089)	0.309 (0.357)	19.4	2
$\text{C}_3 + \text{C}_4$	-0.001	0.005	0.3	
$\text{C}_3 + \text{C}_6$	0.020 (0.019)	0.062 (0.061)	3.5	
$\text{C}_3 + \text{C}_8$	0.054	0.154	8.2	
$\text{C}_3 + \text{C}_{10}$	0.067 (0.089)	0.253 (0.287)	12.7	
$\text{C}_4 + \text{C}_6$	0.013	0.027	1.4	
$\text{C}_4 + \text{C}_8$	0.047	0.104	4.7	3
$\text{C}_4 + \text{C}_{10}$	0.067	0.201	8.6	4
$\text{C}_6 + \text{C}_8$	0.012	0.026	0.9	
$\text{C}_6 + \text{C}_{10}$	0.036 (0.037)	0.096 (0.098)	3.2	5
$\text{C}_8 + \text{C}_{10}$	0.009	0.023	0.6	6

^a The excess properties refer always to the equimolar composition. Calculated values were obtained using flory theory. In the alcohol mixtures (ref 9), the V^E values were estimated from H^E experimental data. The values between brackets correspond to H^E values estimated in this work from V^E experimental data, also from ref 9 (see text).

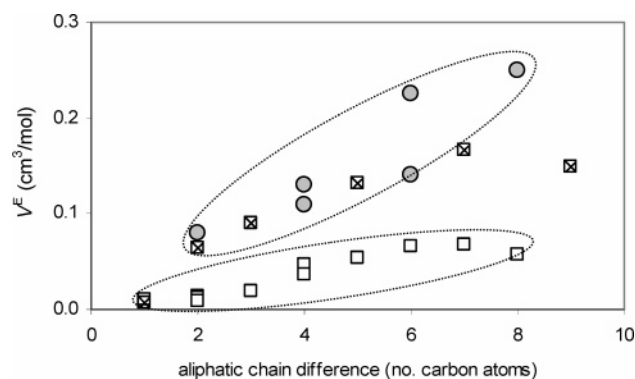


Figure 2. Excess molar volume at the equimolar composition as a function of the aliphatic chain length difference, $|m - n|$, between components: $[\text{C}_m\text{mim}] + [\text{C}_n\text{mim}][\text{NTf}_2]$ (circles) and $\text{C}_m\text{OH} + \text{C}_n\text{OH}$ (squares) systems. The crossed squares refer to alcohol mixtures containing methanol.

(both in absolute or relative terms) is greater than in those mixtures only including longer alcohols. As in many other cases, the behavior of the smallest members of a given homologous family does not fall into the general trend of the other members.

Comparison with Mixtures of Inorganic Molten Salts. The volumetric behavior of some mixtures of inorganic molten salts with a common cation or anion is also comparable to that of the IL mixtures under discussion. For instance, some mixtures of molten alkali halides also show small, positive V^E values, which are symmetric with respect to composition and increase with the difference in the ion size.¹⁰ Similarities between the

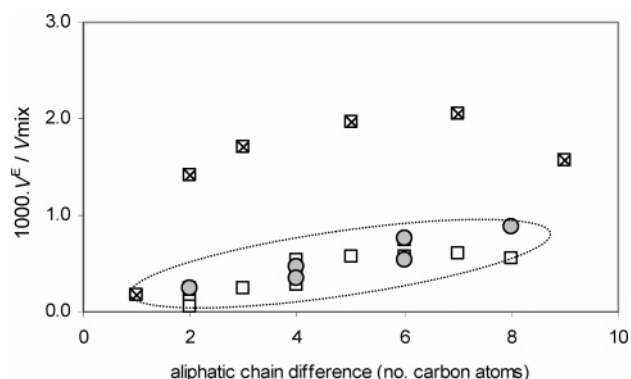


Figure 3. Reduced excess molar volume at the equimolar composition as a function of the aliphatic chain length difference between components, $|m - n|$, in the $[\text{C}_m\text{mim}] + [\text{C}_n\text{mim}][\text{NTf}_2]$ and $\text{C}_m\text{OH} + \text{C}_n\text{OH}$ systems. Markers as in Figure 2.

two types of system are easy to establish since both inorganic molten salts and ILs exhibit strong electrostatic interactions. However, we think that the analogy between molten inorganic salts and the IL systems now under discussion (the “ $[\text{C}_m\text{mim}]^+ + [\text{C}_n\text{mim}]^+$ ” mixtures) is not as striking as that between the latter and linear alcohols because when the cation is changed in these mixtures the charged part (the imidazolium cation residue) remains intact and merely the length of the aliphatic chain is changed. In other words, both in the “ $[\text{C}_m\text{mim}]^+ + [\text{C}_n\text{mim}]^+$ ” and alcohol mixtures one observes aliphatic chains of variable length attached to an electrostatic (in the ILs) or hydrogen-bonded (in the alcohols and ILs) matrix that remains

unaltered from mixture to mixture. This is not the case of inorganic molten salts mixtures (or in the mixtures of ILs with different anions), where the nature of the electrostatic matrix changes between the different mixtures in the series.

Interpretation Using Flory's Theory. The comparison can be taken even further if one takes into account the Flory theory of mixtures.¹¹ This theory has been useful in interpreting the results of measurements of the excess properties of a number of binary systems formed by molecular species that differ in size and shape. Although in the development of the theory, hydrogen bonds and interactions of strong electrostatic nature are specifically excluded, a purely empirical application of the Flory formalism can still provide an interesting correlation between the excess volumes and excess enthalpies of more complex mixtures. In fact, and despite the ionic character of the IL systems, the use of Flory-type theories has proven successful in predicting and modeling both the excess properties and fluid-phase behavior of IL-containing mixtures.^{8,12,13} The same is valid for the alcohol systems.⁹ In the remainder of this discussion, the Flory theory is briefly reviewed and its application to our results is described. Other theoretical models particularly suited to systems with charged particles, for instance the restricted primitive model (RPM) or the mean spherical approximation (MSA) will not be considered in this paper owing to (i) the nonspherical nature of the ions of the IL; (ii) the constancy of the electrostatic interactions along the “ $[(C_m\text{mim})^+ + [C_n\text{mim})^+]$ ” series, as discussed above; and (iii) the fact that the trends along the homologous series of “ $[(C_m\text{mim})^+ + [C_n\text{mim})^+]$ ” and linear alcohol mixtures can be attributed to the variation of the length of the aliphatic (noncharged) chain of each pure component.

According to Flory theory, the excess molar enthalpy and molar volume of a binary mixture composed of molecules that differ regarding the number of segments (isometric portions), r , each containing s interacting sites are given by:⁹

$$H_{\text{Flory}}^E = x_1 p_1^* v_1^* (\tilde{v}_1^{-1} - \tilde{v}^{-1}) + x_2 p_2^* v_2^* (\tilde{v}_2^{-1} - \tilde{v}^{-1}) + x_1 v_1^* \theta_2 X_{12} \tilde{v}^{-1} \quad (1)$$

and

$$V_{\text{Flory}}^E = (x_1 v_1^* + x_2 v_2^*) (\tilde{v} - \phi_1 \tilde{v}_1 - \phi_2 \tilde{v}_2) \quad (2)$$

where x is the mole fraction, p^* and v^* are the characteristic pressure and molar volume, respectively, \tilde{v} is a reduced volume, θ and ϕ are segment and site fractions, respectively, and X_{12} is the so-called cross interaction parameter. The 1 and 2 subscripts refer to the two pure components, whereas quantities without a subscript refer to the mixture.

For a given pure component at a given temperature, the characteristic pressure and molar volume, p_i^* and v_i^* , and the reduced volume, \tilde{v}_i , can be obtained from the experimental vapor pressure and orthobaric density data together with the knowledge of the isothermal compressibility and thermal expansion coefficients of the liquid, β_T and α_p , respectively.^{9,11} The values of β_T and α_p for all the ILs contained in the mixtures under discussion in this work were assumed to be similar to the experimental data available for a few of them.^{2,8,13} More specifically, this type of IL exhibits, for instance, at room temperature and ambient pressure, β_T values ranging from $(3.5\text{--}5.5) \times 10^{-5} \text{ bar}^{-1}$ and α_p from $(5.5\text{--}6.5) \times 10^{-4} \text{ K}^{-1}$.

On the other hand, the θ_2 and ϕ_i variables are functions of r and s , which in turn are related to the molar volume ratio between the two pure components. This means that if either

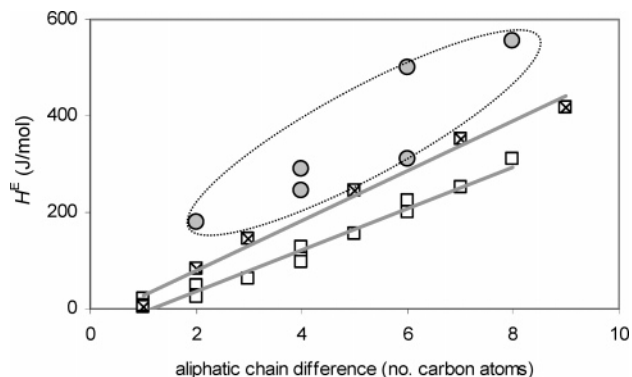


Figure 4. Excess molar enthalpy at the equimolar composition as a function of the aliphatic chain length difference between components, $|m - n|$, in the $[(C_m\text{mim}) + [C_n\text{mim})][\text{NTf}_2]$ and $(C_m\text{OH} + C_n\text{OH})$ systems. Markers as in Figure 2.

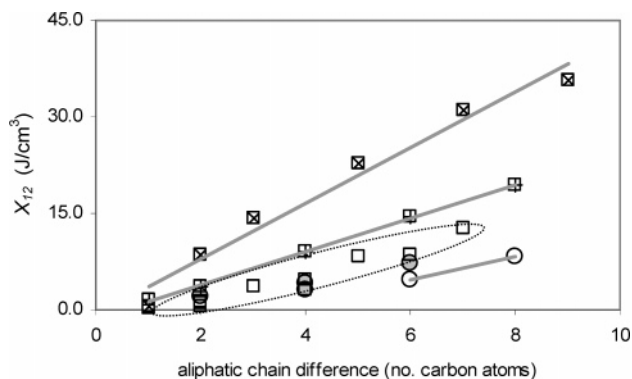


Figure 5. Cross interaction parameter (Flory theory) as a function of the aliphatic chain length difference between components, $|m - n|$: $[(C_m\text{mim}) + [C_n\text{mim})][\text{NTf}_2]$ (circles) and $(C_m\text{OH} + C_n\text{OH})$ (squares) systems. The crossed and “plus” squares refer to alcohol mixtures containing methanol and ethanol, respectively. The two open circles refer to IL systems containing $[C_2\text{mim}]^+$.

the excess molar volume or enthalpy of a mixture is known, the other excess property and X_{12} can be obtained using the theory. In the case of mixtures of linear alcohols, the experimental values of H^E were used to calculate V^E and the latter quantity was compared with experimental results;⁹ in our case, the experimental V^E data were used to estimate the experimentally unavailable H^E values. A brief description of the calculation procedure can be summarized: (i) an experimental V^E value taken at a known composition is introduced in eq 2 and the reduced volume of the mixture, \tilde{v} , is calculated (all other variables are obtained using the properties of the pure components of the mixture and its composition); (ii) the reduced temperature of the mixture, \tilde{T} , is obtained from \tilde{v} using an appropriate reduced equation of state (eq 4 of ref 9); (iii) X_{12} is then obtained using the Flory expression that relates the reduced temperature of a mixture with the value of X_{12} (eq 4 of ref 9); (iv) finally, the H^E value can be estimated using eq 1 since now both \tilde{v} and X_{12} are known. This calculation procedure was tested using experimental V^E values (listed in ref 9 for ten different alcohol mixtures) to estimate the corresponding H^E values. These compared favorably with the experimental H^E data presented in the same paper.

In Table 3 and Figure 4, we present the calculated H^E values of the IL mixtures and compare them with H^E experimental values for the alcohol systems. The calculated alcohol H^E values mentioned at the end of last paragraph were also included in Table 3. All calculations and comparisons are made at the equimolar composition. Again, the analogy between the behavior of IL and alcohol systems is obvious.

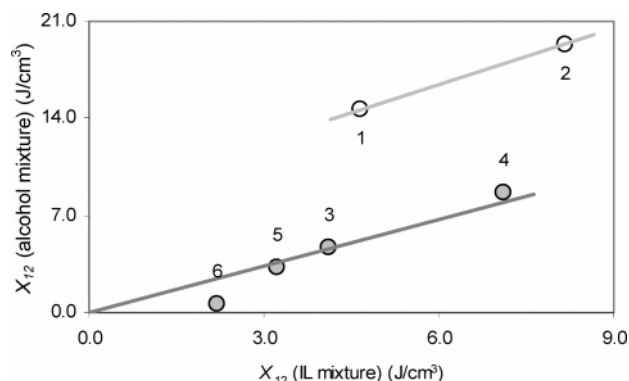


Figure 6. Cross interaction parameter (Flory theory) in the alcohol binary mixtures against the same parameter in the analogous IL systems. The numeric labels refer to the systems designated by the same number in Table 3. The open circles refer to systems comprising ethyl chains in one of the components, the shaded circles to mixtures containing only longer aliphatic chains.

A more relevant way to quantify the deviations from ideality of a given mixture is to estimate its excess Gibbs energy. Within the framework of Flory-type theories, that quantity can be accessed via the calculation of the X_{12} interaction parameter. In Figure 5, the values of X_{12} for the IL and alcohol mixtures are plotted. Here, new trends emerge within the IL and alcohol families: mixtures containing methanol continue to deviate significantly from the X_{12} trend observed for the other alcohol mixtures, while mixtures containing ethanol also deviate slightly from the behavior exhibited by mixtures of the longer alcohols. In the IL mixtures, those containing $[C_2mim]^+$ also show a different trend in terms of the X_{12} parameter when compared with mixtures of $[C_nmim]^+$ with longer side alkyl chains.

Interestingly, the values of X_{12} as a function of chain length difference are very close for IL and alcohol mixtures containing long aliphatic chains. This fact is emphasized in Figure 6, where the values of X_{12} for the alcohol systems are plotted against those for the analogous IL systems: for instance, the (butanol + decanol) system is plotted against the $([C_4mim] + [C_{10}mim])$ - $[NTf_2]$ system. The analysis of both Figures 5 and 6 clearly shows that the cross interaction parameter for the IL binary mixtures increases as the size difference between the cations does, potentially leading to liquid–liquid phase separation conditions.⁴

The systems (both IL and alcohol) containing longer aliphatic chains fall close to a trend-line that was forced to pass through the origin and has a slope close to unity, i.e., the values of X_{12} for analogous systems are similar. The behavior of the systems containing chains with two carbons (ethanol and $[C_2mim][NTf_2]$) fall into a completely different trend-line, showing that the interactions of the longer alcohols with ethanol and the longer ILs with $[C_2mim][NTf_2]$ are of a different nature; no longer just alkane–alkane interactions but also alkane–polar residue interactions.

Interpretation Using the Principle of Congruence. This last fact can be confirmed using the so-called congruence principle, as developed by Koeft and Hijmans,¹⁴ for studying thermodynamic properties along a homologous series of compounds (for instance, those that differ in the length of an aliphatic chain). The principle states that, if the equilibrium properties of a mixture of two homologous components are represented as a function of the average size of the chain length, $n = n_1x_2 + n_2x_1$, then two mixtures with the same n are called congruent if there is correspondence between their properties. In other words, the congruence principle is a graphical method that can

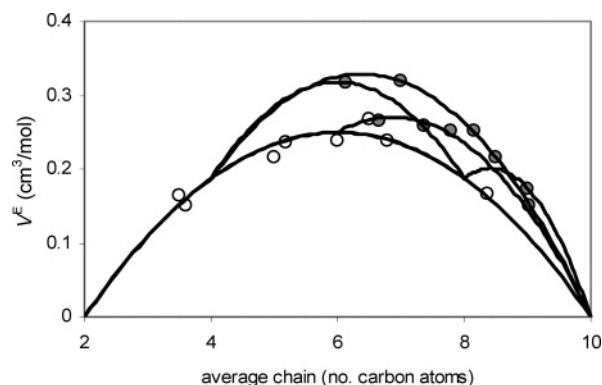


Figure 7. Application of the congruence principle to the $([C_m\text{mim}] + [C_n\text{mim}])[NTf_2]$ mixtures: Congruent molar excess volume as a function of average chain length, using as reference system the $([C_2mim] + [C_{10}mim])[NTf_2]$ mixture. The open circles refer to systems comprising $[C_2mim][NTf_2]$, the shaded circles to mixtures containing longer aliphatic chains in both components.

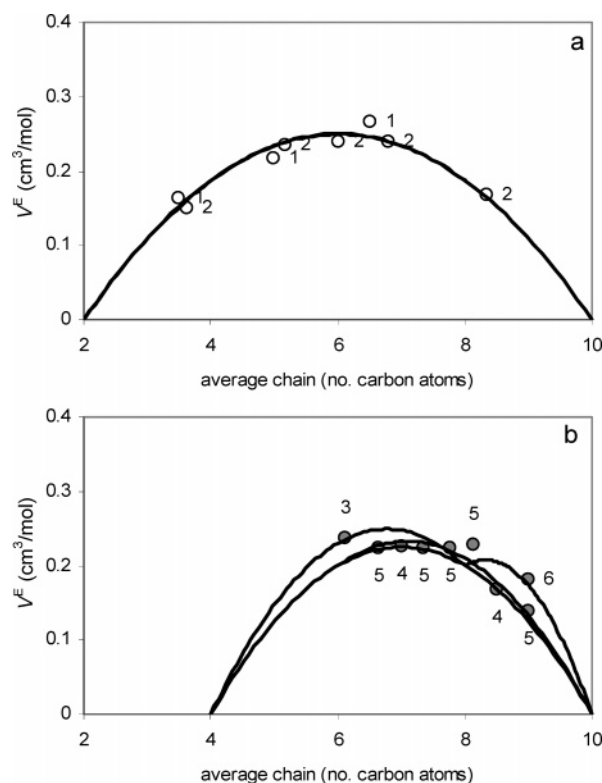


Figure 8. Congruent molar excess volume as a function of average chain length, using as reference system the (a) $([C_2mim] + [C_{10}mim])$ - $[NTf_2]$ or (b) $([C_4mim] + [C_{10}mim])$ - $[NTf_2]$ mixtures. Markers as in Figure 7.

map the representation of the thermodynamic properties of one mixture (in our case the excess molar volume) into those of a reference system. The equation that produces such transformation is simply given by

$$V^E(n, n_1, n_2) = V^E(n, n_A, n_B) - \frac{n_2 - n}{n_2 - n_1} V^E(n_1, n_A, n_B) - \frac{n - n_1}{n_2 - n_1} V^E(n_2, n_A, n_B) \quad (3)$$

where the subscripts 1, 2, A, and B applied to n refer to the chain length of components 1 and 2 in the mixture to be transformed while components A and B belong to the reference mixture. The first argument of the V^E function states the average

chain length at which V^E is evaluated, while the second and third arguments refer to the original representation of the mixture (n_1, n_2) or to its representation in terms of the reference system (n_A, n_B).

In Figure 7 the congruence principle is applied to the representation of the excess molar volume for the different IL mixtures studied, using as reference the mixture with the larger difference in side-chain length ($[C_2mim] + [C_{10}mim]$) $[NTf_2]$. It is clear that the experimental data all lie within a broad symmetric parabola, confirming the additive trend observed for this property. Nevertheless, one can also observe that, whereas the two systems containing $[C_2mim][NTf_2]$ lie on the same parabola (they have a completely congruent behavior), the systems containing longer chain ILs lie slightly above that curve and show greater scattering when mapped onto the “ $(C_2 + C_{10})$ ” system.

To test the observation that in fact we have two congruent families (mixtures with and without $[C_2mim][NTf_2]$ as one of the components), the principle was also applied using the “ $(C_4 + C_{10})$ ” mixture as reference. The results are shown in Figure 8a and 8b, where the two congruent families are depicted separately. It can be seen that by separating the mixtures into these two families, the data in each group comply much better with the congruence principle.

4. Conclusions

The systems under investigation form homogeneous binary liquid mixtures. They constitute a particularly interesting situation for any observed excess effect is a consequence of the emerging interactions of two distinct anions (or cations) in the field of a constant cation (or anion). Therefore, somewhat surprisingly, both experimental evidence and theoretical estimates reveal a *quasi*-ideal behavior, which, nonetheless, becomes increasingly nonideal as the size difference between the cations rises. This relationship is quantitatively well correlated, as also happens when comparisons are made with analogous situations found in linear alcohols binary mixtures.

Despite the inherent molecular-ion complexity of these IL mixtures (electrostatic, van der Waals, and hydrogen-bonded interactions), it seems that in many situations their behavior can be successfully rationalized as if they were “simpler” systems. This may be due to a “cancellation” or “screening” effect. Hence, the similarity found in this study with the family of linear alcohols, as well as the use of Flory’s theory for a semiquantitative interpretation of the results. In regard to this latter point, unfortunately, and to the best of our knowledge, there are neither experimental values of H^E nor independent information on χ_{12} of (IL(1) + IL(2)) mixtures to challenge the soundness of the simple theoretical approach employed here. Anyhow, our theoretical estimates clearly show that an enhancement in the size difference of the ILs might lead to phase separation, in accordance with some preliminary experimental evidence.

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