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Assessing the Dispersive and Electrostatic Components of the Cohesive Energy of Ionic Liquids Using Molecular Dynamics Simulations and Molar Refraction Data

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Molecular dynamics simulations were used to calculate the density and the cohesive molar internal energy of seventeen different ionic liquids in the liquid phase. The results were correlated with previously reported experimental density and molar refraction data. The link between the dispersive component of the total cohesive energy of the fluid and the corresponding molar refraction was established in an unequivocal way. The results have shown that the two components of the total cohesive energy (dispersive and electrostatic) exhibit strikingly different trends and ratios along different families of ionic liquids, a notion that may help explain their diverse behavior toward different molecular solutes and solvents.

Introduction

In a recent work,[1] density and refractive index data were used to calculate the molar refraction of 17 ionic liquids that were representative members of four distinct families of ionic liquid (see Scheme 1 of ref 1). Molar refraction data are typically associated with molecular characteristics such as polarizability or hard-core volume through the Clausius–Mossotti or Lorentz–Lorenz equations.[2,3] However, special care must be taken when such relations are applied to ionic liquids since in this case most of the assumptions underlying their use—isotropic fluids composed of spherical, noninteracting particles—make no sense from a physical perspective: ionic liquids are built from strongly interacting nonspherical ions with quite diverse shapes and are nanosegregated, nonisotropic fluids composed of a polar network permeated by nonpolar domains. We have shown[1] that although such correlations can sometimes yield correct values, for instance, of the solubility of a given solute within a homologous series of ionic liquids,[4] they should not be generalized, as they have no proved physical meaning.

It was also stressed[1] that regardless of these difficulties the correlation of physical properties using molar refraction data should not be abandoned. Apart from the above-mentioned "local" correlations, one could also envisage a method using molecular simulation where the dispersive contribution (a measure of the average molecular polarizability, as expressed by the London equation) could be isolated from the overall interactions within the fluid and correlated to the existing molar refraction data. This new line of investigation is the main focus of the present work.

Molecular Simulation

The molecular force field used in the simulations of the 17 ionic liquids studied in this work is based on the CLaP force-field.[5–8] Following the spirit of OPLS-AA model,[9] covalent bonds and angles are taken from the AMBER force field,[10] and efforts are focused on carefully describing conformational and intermolecular terms. The latter include Coulomb interactions defined in terms of atomic point charges while the repulsive and dispersive contributions are described by the Lennard-Jones 12-6 potential. Details concerning the development and implementation of the force-field can be found elsewhere.[5]

All simulations were performed using molecular dynamics, implemented using the DL_POLY code.[11] The acronyms used throughout the text are the following: $[C_n mim]$ and $[P_{6\ 6\ 6\ 14}]$ represent the 1-alkyl-3-methylimidazolium and trihexyl(tetradecyl)phosphonium cations, $[Ntf_2]$, $[PF_6]$, $[Otf]$, $[Oac]$, $[MeSO_4]$, and $[BF_4]$ represent the bis(trifluoromethylsulfonyl)amide, hexafluorophosphate, triflate, acetate, methyl sulfate, and tetrafluoroborate anions, respectively. In the case of the ionic liquids $[C_n mim][NTf_2]$, where *n* is 2, 4, 6, 8, 10, 12, and 14, $[C_4 mim][BF_4]$, and $[C_n mim][PF_6]$, where *n* is 4, 6, and 8, we started from low-density initial configurations composed of 150 ion pairs. For $[C_4 mim]$-$[MeSO_4]$ we used 250 ion pairs, while for $[C_4 mim][OAc]$, $[C_4 mim][Otf]$, $[P_{6\ 6\ 6\ 14}][Ntf_2]$, $[P_{6\ 6\ 6\ 14}][Oac]$, and $[P_{6\ 6\ 6\ 14}][OTf]$ the systems contained 200 ion pairs. These differences in the total number of ion pairs reflect the distinct molar volumes of the various ionic liquids and the need to use cubic simulation boxes with sides of at least 3.5 nm. The boxes were equilibrated in isothermal–isobaric ensemble conditions for 500 ps at 300 K using the Nosé–Hoover thermostat and isotropic barostat with time constants of 0.5 and 2 ps, respectively. The equilibrium density was attained after about 50 ps. Further simulation runs of 100 ps were used to produce equilibrated systems at the studied temperatures. Electrostatic interactions were treated using the Ewald summation method considering six reciprocal-space vectors, and repulsive-dispersive interactions were explicitly calculated below a cutoff distance of 1.6 nm (long-range corrections were applied assuming the system has an uniform density beyond that cutoff radius). Finally, 1000 configurations were stored from production runs of 300 ps (with 2 fs time steps) for each one of the ionic liquids. Four successive 300 ps runs showed no drift in the corresponding equilibrium properties

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TABLE 1: Experimental Density, ρ_{exp}, Refraction Index, n_{exp}, and Molar Refraction, $R_{m,exp}$, Data, and Simulated Density, ρ_{sim}, and Cohesive Energy, $U_{cohesive,sim}$, Values of Four Families of 17 Ionic Liquids, at 298 K and 1 bar Nominal Pressure[1] [a]

ionic liquid	ρ_{exp}, g/cm³	ρ_{sim}, g/cm³	n_{exp}	$R_{m,exp}$, cm³/mol	$U_{cohesive,sim}$ kJ/mol		
					tot	vdw	coul
[C₂mim][Ntf₂]	1.515	1.58	1.4225	65.7	171	89	81
[C₄mim][Ntf₂]	1.436	1.50	1.4265	74.9	178	99	79
[C₆mim][Ntf₂]	1.371	1.43	1.4295	84.2	183	108	76
[C₈mim][Ntf₂]	1.319	1.36	1.4326	93.6	187	114	73
[C₁₀mim][Ntf₂]	1.278	1.31	1.4356	102.9	197	126	71
[C₁₂mim][Ntf₂]	1.245	1.27	1.4376	112.0	205	135	70
[C₁₄mim][Ntf₂]	1.201	1.24	1.4346	121.5	215	147	68
[C₄mim][PF₆]	1.364	1.33	1.4084	51.5	184	68	116
[C₆mim][PF₆]	1.292	1.25	1.4165	60.7	192	78	114
[C₈mim][PF₆]	1.234	1.21	1.4235	70.3	200	88	112
[P₆ ₆ ₆ ₁₄][Ntf₂]	1.065	1.07	1.4496	192.6	267	200	67
[P₆ ₆ ₆ ₁₄][Otf]	0.982	1.00	1.4577	175.7	256	186	71
[P₆ ₆ ₆ ₁₄][Oac]	0.891	0.91	1.4818	173.6	280	183	97
[C₄mim][OTf]	1.299	1.34	1.4366	58.1	179	86	94
[C₄mim][MeSO₄]	1.211	1.19	1.4777	58.4	199	94	105
[C₄mim][BF₄]	1.199	1.16	1.4215	47.8	180	64	117
[C₄mim][Oac]	1.053	1.08	1.4938	42.1	279	71	208

[a] Total (tot) $U_{cohesive,sim}$ values are divided into their dispersive (vdw) and Coulomb (coul) terms.

and selected pair radial distribution functions at this stage. Furthermore, simulations of the vapor phase were carried out considering it is formed by isolated neutral ion pairs, an assumption based on experimental evidence[12] for this type of ionic liquids. These were equilibrated in canonical ensemble ($N−V−T$) conditions for 40 ns at 300 K using the Nosé−Hoover thermostat with a time constant of 1.0 ps. Electrostatic interactions were treated using the Ewald summation method considering six reciprocal-space vectors, and repulsive-dispersive interactions were explicitly calculated below a cutoff distance of 500 Å. Since the statistics are poor due to the small number of atoms, each production run took 40 ns and 10 such runs were used to calculate the average gas-phase properties.

Results and Discussion

The simulation trajectories for each pure ionic liquid were used to calculate the total molar cohesive internal energy of the liquid phase, U_{tot}, by subtracting the total configuration energy of 1 mol of ion pairs in the vapor phase from the total configuration energy of one mole of ion pairs in the liquid phase. In this way the configuration energy corresponding to the internal binding and conformational energies of the molecules (from bonds, angles, dihedral angles, and internal nonbonded interactions) were not taken into account. Moreover, the U_{tot} was decomposed into its Coulomb, U_{coul}, and dispersive, U_{vdw}, contributions by considering separately the configuration energy differences of the respective force-field terms. The results are presented in Table 1, along with the previously published density, refraction index, and molar refraction data.[1] The simulated densities are also given in the table and confirm the adequate modeling of the different ionic liquids under analysis.[5]

To check that the molar refraction is a measure of the overall molecular polarizability, related to the importance of the dispersion forces in the condensed phase, plots of R_m versus U_{tot} and U_{vdw} were produced and are presented in Figure 1. The figure clearly shows that the molar refraction of distinct families of ionic liquids can be correlated to the dispersive component of their molar cohesive energies, but not to the total molar cohesive energies. This simple illustration confirms the well-known fact that molar refraction is strongly correlated with molecular polarizability and in the case of ionic liquids can be regarded as a measure of the dispersion forces within the fluid. In other words, Coulomb interactions should not be tallied when
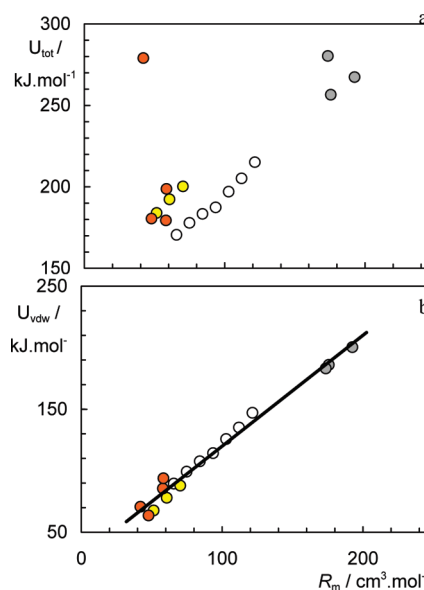

Figure 1. (a) Total molar cohesive energy, U_{tot}, and (b) its van der Waals contribution, U_{vdw}, as a function of the molar refraction of the 17 ionic liquids under discussion. The colors correspond to the four families of ionic liquids (cf. Table 1 and Figure 2).

dealing with correlations involving molar refraction. It must be stressed that in the present force-field model the U_{vdw} term corresponds only to the interactions resulting from the Lennard-Jones interatomic potential (a $1/r^{12}$ soft-core repulsive term plus a $1/r^6$ attractive London dispersion term). No (permanent-dipole)−dipole interactions are considered explicitly in the present force field, with all electrostatic interactions (including the implicit presence of molecular dipoles or hydrogen bonding, which are handled by the positioning of electric point charges at the interaction centers of the ions) being accounted for in the U_{coul} term. This means that, like R_m, the U_{vdw} terms are related to the mean electronic polarizability of the media, but not the U_{coul} (or U_{tot}) terms.

The figure also illustrates why it is not physically sound to correlate properties such as gas solubility in ionic liquids with molar refraction data: the former property depends on the different types of interaction present in the ionic liquid (van der Waals and electrostatic), while the latter are related with the dispersion forces only. The possibility of using such

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correlations in a more limited manner, for some (but not all) homologous families of ionic liquids, is also apparent in Figure 1a: almost linear (but distinct) trends can be observed between the total molar cohesion energy and the molar refraction data for $[C_n mim][Ntf_2]$ and $[C_n mim][PF_6]$ ionic liquids. In contrast, no obvious correlations exist for ionic liquids based on the $[P_{6\ 6\ 6\ 14}]$ and $[C_4 mim]$ cations with different anions. In the former case, one has two homologous series where as the alkyl-side-chain length increases, the van der Waals forces increase in a regular manner while the Coulomb forces stay almost constant, as shown in the white and yellow series of Table 1. In other words, the total cohesive energy change along the series only reflects changes in the van der Waals interactions; the highly charged parts of the ions and their electrostatic interactions remain unchanged. In the latter case one can no longer consider homologous series because the charged parts of the ionic liquid and their Coulomb forces change considerably when one anion is exchanged for another. These changes will impact considerably properties like the solubility but will not affect the molar refraction of the medium. Correlation between these two quantities will be poor and will not lead to meaningful predictions (cf. Figure 1a).

The correlation between the experimental molar refraction data and the simulated dispersive contribution to the total energy of the different ionic liquids can be seen as a supplementary validation of the CLaP model. Although the cohesive energies are slightly overestimated by the model when compared to available experimental data (e.g., vaporization enthalpy values of $150-250$ kJ mol^{-1} compared with $120-200$ kJ mol^{-1} determined by a direct method[12,13]), such a difference, acceptable in a purely predictive model, does not perturb the strong correlation between R_m and U_{vdw}. It must be noted that the vaporization enthalpies, ΔH_{vap}, can be readily calculated from the presented cohesive energies if one assumes the ideality of the gas phase: $\Delta H_{vap} = U_{gas} - U_{liquid} + pV = U_{cohesive} + RT$.

Even when the simulated results are refined to fit experimental vaporization data,[14] the correlation should remain valid, as well as the ratio between the electrostatic and dispersive contributions. This can be corroborated by other simulation results found in the literature, where the van der Waals and Coulomb contributions to the total cohesive energy of different ionic liquids were calculated using different force field models. For instance in the case of $[C_2 mim][NTf_2]$, Kelkar and Maginn[15,16] used their own force field for dialkylimidazolium cations to estimate a vaporization enthalpy of 146 kJ mol^{-1} with similar contribution from the dispersive and electrostatic terms (both 74 kJ mol^{-1}),[15] whereas in the case of $[C_4 mim][PF_6]$, the contribution from the Coulomb terms is much larger (approximately the double) to the total cohesive energy.[16] Another example showing the independence of the correlations in regard to the type of force field used can be found in the work of Raabe and Köhler[17] that used an united-atom force field and predicted a vaporization enthalpy of 183 kJ mol^{-1} with contributions of 110 and 62 kJ mol^{-1} from the Coulomb and van der Waals interactions, respectively. These trends in the decomposition of the total cohesive energy are consistent with the ones observed in our study that used the same systematic force-field to analyze the behavior of the 17 ionic liquids (grouped into four classes and including two homologous series) studied in this work. Our predicted decomposition of the total cohesive energy into van der Waals and Coulomb terms is represented in Figure 2.

The contributions from the dispersive and electrostatic interactions (green and red in Figure 2, respectively) to the total energy depend dramatically on the nature of the ions. Very large
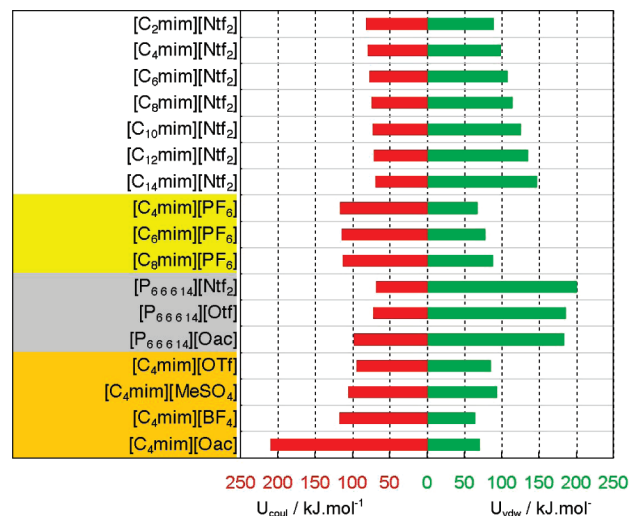

Figure 2. Electrostatic (red), U_{coul}, and dispersive (green), U_{vdw}, components of the molar cohesive energy of the 17 ionic liquids under discussion. The ratios of the two quantities, $U_{coul}:U_{vdw}$, can be as large as 4:1 in $[C_4 mim][Oac]$ or as low as 1:3 in $[P_{6\ 6\ 6\ 14}][Ntf_2]$ (cf. discussion).

ions such as tetraalkylphosphonium cations originate disproportionate dispersive contributions. Strongly basic anions like acetate yield large electrostatic contributions when combined with cations that can provide several acidic hydrogen atoms (e.g., imidazolium-based cations).

These different dispersive/electrostatic energy ratios are directly related to the polar/nonpolar character of ionic liquids[18] and can explain the diverse behavior toward different solutes or solvents of this class of compounds.[19] For instance, in the case of carbon dioxide dissolved in $[C_n mim][Ntf_2]$ ionic liquids ($n = 2-10$), the mechanism of solvation is known to be controlled by electrostatic-specific interactions and only to a minor extent by free-volume effects.[20,21]

Two final remarks are worth mentioning at this stage. First, molar refraction is a quantity that is strongly dependent on the molar volume, V_m, of the substance.[2] This means that a good correlation can be obtained between U_{vdw} and V_m, similar to that of Figure 1b. This is not surprising in the case of the studied ionic liquids since most are composed of a large proportion of hydrogen and second-period-element atoms (B, C, N, O, F). The latter exhibit similar polarizabilities and similar contributions to the molar volume of the ionic liquid. In cases where heavier elements represent a larger proportion of the overall volume (not just the odd phosphorus or sulfur atom) the correlation between U_{vdw} and V_m will be broken. It is also interesting to notice that recent correlation schemes between vaporization enthalpies and V_m[22] reach conclusions similar to those in this work, namely the necessity to decompose the total enthalpy values into Coulomb and van der Waals contributions, although their decomposition based on the estimation of U_{coul} using a Kapustinski-like scheme does not yield a good correlation between U_{vdw} and V_m. Second, if the cohesive energies are calculated considering isolated ions in the gas phase instead of ion pairs, the correlation between U_{vdw} and R_m is slightly less precise. This suggests that the condensed phase of an ionic liquid should not be regarded as a uniform mixture of anions and cations (like in an inorganic salt lattice) but rather as an interchanging collection of ion pairs, where each cation or anion is surrounded by ions of opposite charge but interacts preferentially with just one or a few of them, in a dynamic "*primus inter pares*" (first among equals) arrangement. This point has been addressed by different simulation works and corroborated by experimental evidence (mainly spec-

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troscopical data but also ionicity studies) where those preferred interactions between a given cation and anion can be related to the formation of hydrogen bonds or other structure-specific interactions.[13,23,24] In fact, many force-fields (including CLaP) have been compared, evaluated, and refined by taking into account their ability to predict the existence of those hydrogen bonds or specific interactions.[13,25]

Many empirical correlations have appeared recently that try to correlate the properties of ionic liquids as solvents or solutes with their characteristic interactions toward a particular molecule. Thus one can easily find series of ionic liquids ordered by their hydrophilicity or hydrophobicity (their relation with water), by their Kamlet–Taft parameters (generally obtained using solvatochromic probes that test their basicity, acidity or dipolarity/polarizability), by their position in an Hoffmeister series (that test their ability as salting-in or salting-out agents), etc.[26] This particular work uses molecular dynamics simulations to estimate the cohesive energy of a pure ionic liquid and decompose it in its dispersive and electrostatic components. Such decomposition is validated by the good correlation between R_m (that is an experimental measure of the dispersive forces within a substance) and the estimated U_{vdw} values. This is the first way to make use of the correlation: to test the force-field model in terms of its ability to correctly decompose the estimated cohesive energy. The second use of the correlations (including the not-so-good one represented in Figure 1a) is to show that the cohesive energy of ionic liquids is a regular function of the molar refraction within a given homologous series of ionic liquids but not between different series. This is something that was already known (hence the term "ionic liquids families") but that was not quantified in terms of the strength of those interactions in the pure ionic liquids. Finally, Figure 2 shows the quite diverse (and somewhat hidden) nature of ionic liquids as regards their cohesive energy: most of them will exhibit estimated cohesive energies in the 170–250 kJ/mol range, but the contributions to those values from the van der Waals and Coulomb interactions can be dramatically different. The use of this intrinsically molecular information in the interpretation and prediction of the behavior of different families of ionic liquids toward different solutes or solvents is a third possible use of the present correlations. A case in point is, for instance, the "out of the fold" character of [C$_4$mim][Oac], as shown in Figures 1a and 2, that can be used to interpret the "extreme" solvent behavior of carboxylate-based ionic liquids toward solutes like cellulose.[26] The much more "polar" character of these ionic liquids and their ability to perform and be part of extended hydrogen-bonded networks certainly plays a role in their ability to interact strongly with a polysaccharide polymer like cellulose.

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