Communication

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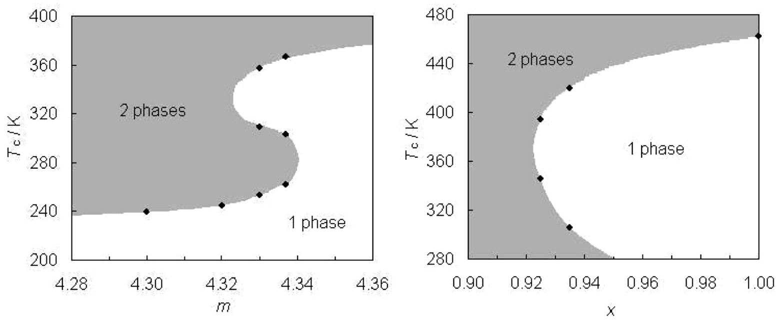

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Since its discovery,[1] the closed-loop type of demixing in liquid solutions has remained a rare phenomenon[2−5] that has triggered debate, stimulated the development of several important applications,[6] and enhanced our understanding of solutions.[7] An intriguing characteristic of this behavior is the attainability of higher order as temperature is increased. In fact, the closed-loop phase diagram emerges as a consequence of a delicate balance between enthalpic and entropic contributions to the Gibbs energy of a mixture. This subtle balance may provoke a two-phase island in a temperature−composition plot at some intermediate range of temperatures above and below which the system is homogeneous (single phase); the novelty lies in the re-entrant homogeneous phase as temperature is decreased. In the language of thermodynamics, this is called a lower critical solution temperature (LCST). We have recently shown,[8] along with others,[9] how solubility phenomena in systems formed by an ionic liquid (IL) with molecular solvents can be surprising and can be profitably used in reaction/extraction processes.

In this work, LCST-type of phase diagrams (usually thought to be restricted to aqueous or polymer solutions) have been encountered for the first time in binary and *quasi*-binary liquid solutions of ILs. Moreover, our results constitute the first experimental support for the existence of a recently theoretically postulated, but never encountered, extraordinary kind[3,10] of type VII phase diagram (system **I**, see below) in an extended version of the celebrated Konynenburg and Scott classification.[11] This is so irrespective of the chemical nature of the mixture. Our evidence is based on binary mixtures of ILs containing the bis{(trifluoromethyl)sulfonyl}amide anion, $[\mathrm{NTf_2}]^-$, with a 1-alkyl-3-methylimidazolium, $[\mathrm{C}_n\mathrm{mim}]^+$ ($1 \leq n$, integer ≤ 18) cation. Specifically, we have discovered ionic liquid−organic solvent systems that (**I**) present either a high-temperature LCST plus a closed-loop [$\mathrm{LCST_1} < \mathrm{UCST} < \mathrm{LCST_2}$][12] in $[\mathrm{C}_m\mathrm{mim}][\mathrm{NTf_2}] + \mathrm{CHCl_3}$ or (**II**) a LCST at a temperature higher than that of the UCST in $[\mathrm{C_5mim}][\mathrm{NTf_2}] + (\mathrm{CHCl_3} + \mathrm{CCl_4})$.[12] Both systems **I** and **II** evolve to the so-called "hourglass" type of phase diagram (merging of the high-temperature LCST with the UCST) upon the manipulation of thermodynamic or pseudo-thermodynamic variables, such as pressure, average length (m) of the cation's alkyl chain of the IL, etc. Figure 1a depicts these situations as temperature−composition plots at a nominal pressure of 1 bar. In case **I**, the solvent is $\mathrm{CHCl_3}$, and the IL is $[\mathrm{C}_m\mathrm{mim}][\mathrm{NTf_2}]$, where $4 \leq m \leq 5$. For example, at $m = 4.33$, there is a closed-loop at low temperature and a high-temperature immiscible region. Therefore, starting at ca. 240 K in the one-phase region and increasing the temperature induces a phase splitting between ca. 260 and 305 K, a homogeneous system between ca. 305 and 370 K, and again a two-phase system above ca. 370 K.

The aforementioned delicate balance (between the excess enthalpy, h^E, and entropy times temperature, Ts^E) can be appreciated by noting that a very subtle change of m from 4.34 to 4.32 has induced the merging of the $\mathrm{LCST_2}$ with the UCST (the same for $m = 4.30$), and the immiscible region is now significantly larger. Conversely, the higher solubility of $[\mathrm{C_5mim}][\mathrm{NTf_2}]$ in $\mathrm{CHCl_3}$ compared to that of $[\mathrm{C_4mim}][\mathrm{NTf_2}]$ implies that for $m = 5.00$ (pure $[\mathrm{C_5mim}][\mathrm{NTf_2}]$), only a very high temperature immiscibility is observed. The subtlety of the phase diagram changes can be better appreciated by using an economical representation (portions b of Figure 1).

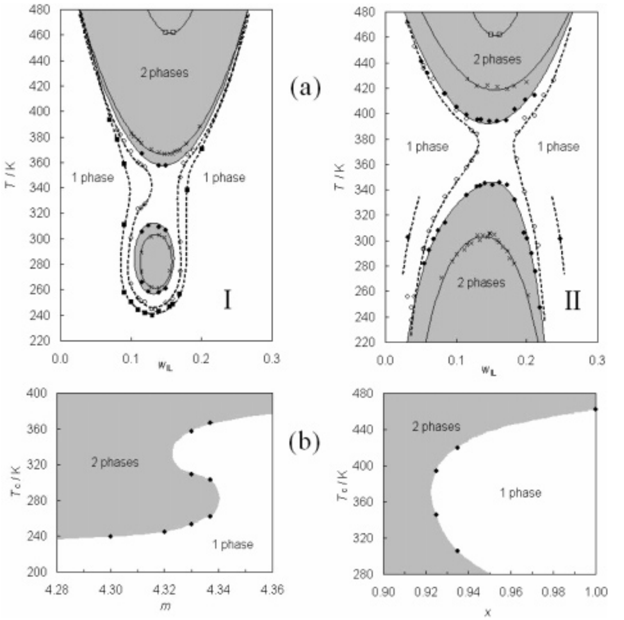

Figure 1. Phase equilibria of $[\mathrm{C}_m\mathrm{mim}][\mathrm{NTf_2}] + \mathrm{CH}_x\mathrm{Cl}_{4-x}$; w_{IL} = weight fraction of IL. In system **I** (left), $x = 1$; (□) $m = 5.000$; (×) $m = 4.337$; (●) $m = 4.330$; (○) $m = 4.320$; (■) $m = 4.300$. The shaded areas depict the demixing regions for $m = 4.330$. In system **II** (right), $m = 5$; c is the weight percentage ratio of $\mathrm{CCl_4}$ in $\mathrm{CHCl_3}$: (□) $c = 0\%$; (×) $c = 6.5\%$; (●) $c = 7.6\%$; (○) $c = 8.0\%$; (◆) $c = 10.5\%$. The hatched areas depict the demixing regions for $c = 7.6\%$. Sections (b) use an economical representation. In case **I**, T_c versus m of $[\mathrm{C}_m\mathrm{mim}][\mathrm{NTf_2}]$; for **II**, T_c versus x of hypothetical $\mathrm{CH}_x\mathrm{Cl}_{4-x}$. The extrema in the one-phase/two-phase borderline correspond to double-critical points where the UCST merges with the LCST.

From a phenomenological perspective, the phase diagrams of Figure 1 imply that the excess properties of the mixture ought to show the trends shown (system **I**) in Figure 2 as temperature is varied. Note that the change of enthalpy, upon mixing, changes sign twice, as dictated by the thermodynamic constraints that exist at the UCSTs and LCSTs. In turn, the excess Gibbs energy shows two temperature ranges where its value is greater (two-phase regions) than the critical one, g_c, and two other temperature ranges where the opposite occurs (one phase). As a consequence, the excess entropy must behave as plotted in the figure. This simple, thermodynamic analysis clearly shows that there are two distinct

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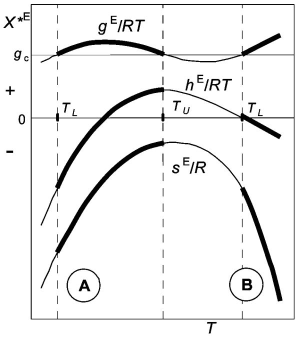

Figure 2. Schematic thermodynamic requirements for the occurrence of the phase diagram of system **I**. X^{*E} is a reduced excess property (Gibbs energy, g^E/RT; enthalpy, h^E/RT; or entropy, s^E/R) of the mixture. Thick portions of the curves hold for the two-phase regions.

mechanisms (A and B) involved in the appearance of each LCST. Beginning at low temperatures, in the vicinity of LCST$_1$, the magnitude of the negative s^E decreases as temperature increases (A), while at high temperatures (LCST$_2$), the trend is the opposite (B). The underlying mechanism of the latter case is the loss of entropy due to the significant contraction of the more volatile component upon its mixing with the IL; this is obviously enhanced as temperature increases. In contrast, at low temperatures (due mainly to the formation of hydrogen bonds between $CHCl_3$ and [C$_m$mim][NTf$_2$], as well as ion-induced dipole interactions), there is a structuring effect responsible for the decrease of entropy, becoming less important as temperature increases. Note that in system **II**, the available hydrogen and chlorine atoms of the "averaged" solvent, CH_xCl_{4-x}, are fine-tuned by mixing precise amounts of $CHCl_3$ and CCl_4.[12]

The hydrogen bonding between unlike species must be brought about by the interaction between the hydrogen of $CHCl_3$ and the π-system of the imidazolium ring together with that between the chlorine atoms and the acidic hydrogen atoms[13] of the same ring, especially the H(2), but also H(4) and H(5); there is accumulating evidence to show that the interactions between $CHCl_3$ and imidazolium-based ILs are significant.[14]

Another important feature of both plots shown in Figure 1 is that, in terms of their abscissae, the "center" of the two-phase regions, which defines the critical composition, corresponds to a relatively low concentration of the IL in the solvent (weight fraction, $w_{IL} \sim 0.15$; mole fraction, $x_{IL} \sim 0.046$). Binary mixtures composed of similar size components present liquid−liquid phase diagrams approximately centered at the equimolar composition. For the value found in this work of $x_{IL} \sim 0.046$, the theoretical[4,15] ratio of sizes, that is, the volume of the larger component over that of the smaller one, is ca. 7.5, which is approximately twice the ratio of molar volumes of IL/$CHCl_3$. Our interpretation is that the bulk of the solution feels, on average, "dimers" of cation−anion contact pairs at concentrations near the critical one. This is strongly supported by the fact that CH_yCl_{4-y} solutions of [C$_2$mim]X (X = Cl, Br, or I) are nonconducting, whereas [NR$_4$]X behave as 1:1 electrolytes. These relatively dilute solutions of IL in $CHCl_3$ present a fluctuating mixture of cation−anion contact pairs, [C$_n$mim][NTf$_2$], with higher aggregates present in equilibrium. Our electrospray mass spectrometric study established the expected presence of $[(C_n\text{mim})_2(\text{NTf}_2)]^+$ and $[(C_n\text{mim})(\text{NTf}_2)_2]^-$ (as well as the component simple cations and anions), in the positive and negative modes for both [C$_4$mim][NTf$_2$] and [C$_5$mim][NTf$_2$] using $CHCl_3$ as the solvent.[14,16]

The aforementioned specific interactions between the IL and $CHCl_3$ are certainly responsible for the exothermic mixing process ($\Delta h = h^E < 0$) at low temperature that these systems have to exhibit as a minimum, although insufficient, requisite for provoking a LCST$_1$-type of demixing. Therefore, a possible key piece of evidence that enables one to anticipate the potential existence of this phenomenon is the increase with increasing temperature of the infinite dilution activity coefficient, γ^∞, of a given solvent in the IL [$-\partial \ln\gamma^\infty/\partial T = h^{E,\infty}/RT^2 < 0$]. One can, thus, anticipate other potential types of IL solutions presenting similar behavior. For instance, solvents with π-clouds, such as benzene, toluene, methylstyrene, etc., must certainly be able to form several kinds of hydrogen bonds and other specific interactions with ILs. In fact, it has been experimentally shown[17] that these diluted solvents in [NTf$_2$]$^-$-based ILs present activity coefficients that increase as temperature increases.

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Supporting Information Available: Experimental section (chemicals, apparatus, mass spectra−ESI); figure (transition temperatures versus pressure); brief thermodynamic remarks. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Definitions: (a) UCST and LCST stand for upper and lower critical solution temperatures, respectively; (b) when a binary mixture of two ionic liquids, [C$_n$mim]Y and [C$_{n'}$mim]Y, is taken, with a mole fraction X_n of the former, it is represented by [C$_m$mim]Y, where $m = nX_n + n'(1 - X_n)$. Similarly, a mixture of CH_yCl_{4-y} and $CH_{y'}Cl_{4-y'}$ is represented by CH_xCl_{4-x}, where $x = yX_y + y'(1 - X_y)$.
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