Why Ionic Liquids Can Possess Extra Solvent Power

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We use the Flory−Huggins theory to demonstrate conditions of extra solvent power of ionic liquids. The short-range interactions between anions, cations, and molecules of the solute are taken into account. We find that solvent power of the ionic liquids is enhanced if non-Coulomb interactions between the anions and cations are repulsive. The mechanism responsible for the extra solvent power is related to the "shielding" of the anion−cation interactions by the molecules of the solute.

Ionic liquids (ILs) are substances solely composed of anions and cations, that are liquid at around (and often below) room temperature.[1,2] The interest in the ILs has significantly increased in the recent years, particularly due to their high potential to be used as reaction media in environment friendly ("green") chemistry. In contrast to conventional molecular liquids, ILs are generally nonvolatile[3,4] at room temperature, and some of them can be distilled only at high temperature and low pressure.[5] Perhaps, the most important peculiarity of the ILs is that they are good solvents for a wide range of both organic and inorganic substances.[1,6,7] Furthermore, various pairs of cations and anions forming an IL can be chosen and thus ILs with desirable properties can be produced.[1,8] That is why unusual combinations of reagents can be brought into the same phase by means of using an IL as a solvent.

For this reason, it seems to be very important to understand the physical reason of IL solvent power. A number of experimental works examined the phase behavior of various mixtures containing IL as one of the components. For example, the effect of the length of alkyl chains of alcohol molecules and of IL cations was studied for various mixtures of imidazole-based ionic liquids and alcohols.[9] Phase diagrams of several binary and ternary mixtures containing ILs were obtained in refs 10−13. Flory−Huggins type theories were worked out in order to fit some of the experimental results.[8,12,13]

To the best of our knowledge, the existing Flory−Huggins type theories treat ILs as ones consisting of molecular entities (or anion−cation pairs). In other words, ILs are considered as "one-component" liquids with the neglect of the difference between anions and cations. On the other hand, in the binary mixtures of ionic and nonionic liquids, interactions of the anions and cations with each other and with the neutral molecules are different. Indeed, fluidity of the ILs is assumed to be provided by a distant location of the charges in neighboring ions due to the presence of a bulky "shell" around each of the charges formed by neutral atoms. Such a shell reduces the energy of electrostatic interactions between the ions which can become less than the energy of thermal motion of the ions at room temperature. It means that the shells can prevent crystallization[14] of the system and provide its fluidity. Therefore, the short-range interactions between the shells of the ions have to be taken into account.

In the present paper, we treat a binary mixture of an ionic and a nonionic liquid as a "three-component" system consisting of anions, cations, and neutral molecules and take into account interactions among all of the components. We will show that the extra solvent power of the ILs can be explained by "incompatibility" of the anions and the cations caused by short-range repulsion of the shells. The physical picture of the effect is the following. If all of the components of a three-component system are neutral, incompatibility between them may result in a macroscopic phase separation which reduces the area of contacts between the components. In the case of ILs, anions and cations cannot be separated macroscopically, because otherwise electric neutrality of the system is violated. Thus, if the incompatibility between the anions and the cations is higher than that between the ions and the neutral molecules, dissolution of the nonionic liquid whose molecules shield unfavorable contacts between the anions and the cations will result in a decrease of the free energy of the system.

Let us consider a spatially homogeneous mixture of an ionic and a nonionic liquid. For the sake of simplicity, we assume that the particles of all of the species have the same size (excluded volume). We believe that examination of the difference in the volumes of the particles does not change the main physical meaning of the effect of extra solvent power. Let Φ_+ and Φ_- be the volume fractions of the cations and the anions, respectively. Then, the volume fraction of the solute is equal to $1 - \Phi_+ - \Phi_-$ (the mixture is assumed to be incompressible). According to the Flory−Huggins theory, the free energy of the system is

$$\frac{f}{kT} = \Phi_+ \ln \Phi_+ + \Phi_- \ln \Phi_- + (1 - \Phi_+ - \Phi_-) \times$$
$$\ln(1 - \Phi_+ - \Phi_-) + \chi_{+-}\Phi_+\Phi_- + \chi_+\Phi_+(1 - \Phi_+ - \Phi_-) + \chi_-\Phi_-(1 - \Phi_+ - \Phi_-) \quad (1)$$

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The first three terms of eq 1 correspond to the entropy of the translational motion of the cations, the anions, and the solute molecules, respectively. We suppose that cations and anions are not coupled into pairs and move independently of each other. The last three terms of eq 1 are responsible for the short-range interactions between the species. They comprise the cation−anion, cation−solute, and anion−solute interactions with the corresponding Flory−Huggins parameters: χ_{+-}, χ_+, and χ_-. It should be noted that the parameter χ_{+-} has nothing to do with the Coulomb interactions of the ions: it describes interactions of the shells of the ions. The mean-field treatment of the system neglects the effects of the density fluctuations. We can expect that the contribution of fluctuation-induced attraction of charged units of the mixture (the Debye−Hückel approach) is small, if inequality

$$l^{3/2}(\Phi_+ + \Phi_-)^{1/2}/R^{3/2} \ll 1 \qquad (2)$$

is held. Here, l is the Bjerrum length, $l = e^2/\epsilon kT$, where the ions are assumed to be monovalent, each of the charge e. ϵ and kT are the dielectric constant of the medium and the thermal energy, respectively; R is the size of the ions. Relying on the distant location of charged units of the neighboring ions (each charged unit is wrapped by a neutral shell), we assume $l \ll R$ which satisfies inequality 2 even under the condition $\Phi_+ + \Phi_- \sim 1$. Therefore, our model neglects the electrostatic interactions. The only consequence of the presence of the ions in the system is a condition of macroscopic electric neutrality which imposes restriction on the values of the fractions Φ_+ and Φ_-. In view of the equal excluded volumes of the cations and the anions, Φ_+ and Φ_- have to be equal to each other:

$$\Phi_+ = \Phi_- = \frac{\Phi}{2} \qquad (3)$$

where Φ is the volume fraction of the ionic liquid. Then, the free energy of the mixture takes the following form:

$$\frac{f}{kT} = \Phi \ln \frac{\Phi}{2} + \chi_{+-} \frac{\Phi^2}{4} + (1 - \Phi)\ln(1 - \Phi) + \chi(1 - \Phi)\Phi \qquad (4)$$

where $\chi = (\chi_- + \chi_+)/2$ is the Flory−Huggins parameter describing interactions of the ionic liquid with the solute. The spinodal toward macrophase separation can be found by a standard procedure, $\partial^2 f/\partial \Phi^2 = 0$, leading to

$$\chi = \frac{1}{2\Phi(1 - \Phi)} + \frac{\chi_{+-}}{4} \qquad (5)$$

The dependence of χ on Φ is represented in Figure 1a for the value of the parameter χ_{+-} equal to 12. Below this curve, a homogeneous mixture of the ionic and nonionic liquid is stable (solubility region). Above this curve, the macroscopic phase separation of the ionic and nonionic liquids occurs.

Let us now consider a mixture of two nonionic liquids whose molecules have the same excluded volume. Let Φ and χ be again the volume fraction of one of the components and the interaction parameter, respectively.

The free energy of such an incompressible system is

$$\frac{f_0}{kT} = \Phi \ln \Phi + (1 - \Phi)\ln(1 - \Phi) + \chi(1 - \Phi)\Phi \quad (6)$$

where the first two terms are the contributions of the translational motion of the molecules of different components and the last
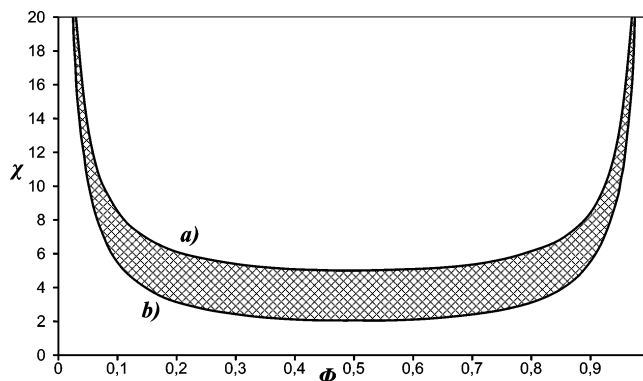

Figure 1. Spinodal of the macroscopic phase separation of a mixture of the ionic and nonionic liquids (a) and of two nonionic liquids (b).

term is responsible for the volume interactions between them. The spinodal value of χ for the two nonionic liquids is

$$\chi = \frac{1}{2\Phi(1 - \Phi)} \qquad (7)$$

It is represented in Figure 1b. Thus, with the decrease of χ, the nonionic liquid is dissolved first in the IL rather than in the equivalent nonionic liquid (the equivalence means that they have the same χ value with respect to the solute). The region of "extra" solubility of the IL is shaded in Figure 1. Its gap, $\Delta\chi$, is determined by incompatibility between the cations and the anions, $\Delta\chi = \chi_{+-}/4$. To increase the solvent power of the IL, one has to take species of ions that are more incompatible.

In conclusion, we have shown that the short-range repulsive interactions between the shells of the anions and cations enhance the solvent power of the ionic liquids. The condition of macroscopic electric neutrality of the ILs prohibits the macroscopic phase separation of the ions. The only opportunity to reduce unfavorable contacts between them is the absorption of the molecules of the coexisting substance(s). In this paper, we do not analyze the effects of segregation of the ions at the finite length scales[15] (an analogue of microphase segregation in polyelectrolyte systems[16]). The results of these studies will be published in a forthcoming publication.

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