

Microphase Separation in a Mixture of Ionic and Nonionic Liquids

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We use a Flory–Huggins type approach and the random phase approximation (RPA) to describe a microphase separation in the mixture of ionic and nonionic liquids. The mixture is modeled as a “three-component” system including anions, cations, and neutral molecules. Each ion is considered to consist of a charged group surrounded by a neutral “bulky” shell. The shells of the anion and cation are assumed to have different affinities to the neutral molecules. We show that, if the difference of the Flory–Huggins parameters describing affinities of the anions and cations to the neutral molecules is higher than a certain value, the microphase separation can occur. The physical reason for the separation is a delicate balance between the short-range segregating interactions and the long-range Coulomb interactions.

Introduction

Ionic liquids (ILs) are substances solely composed of anions and cations that are liquid at around (and often below) room temperature.^{1,2} ILs are generally nonvolatile^{3,4} at room temperature. Some of ILs can be distilled only at high temperature and low pressure.⁵ It makes ILs different from other conventional nonionic solvents. Due to this feature and to a number of other unique properties, ILs have a high potential to be used as reaction media in environmentally friendly (“green”) chemistry. For this reason, an interest in ILs has significantly increased in recent years.

Another important property of ILs is that they can dissolve a wide range of both organic and inorganic substances^{1,6,7} and, simultaneously, have excellent chemical and thermal stability. It is possible to choose different pairs of cations and anions when composing an IL. This allows production of ILs with predefined properties^{1,8} capable of dissolving combinations of reagents that cannot be dissolved simultaneously in an ordinary molecular solvent. In our recent publication,¹³ we proposed a possible explanation for the physical reason for the high solvent power of the ILs.

ILs mix not with all liquids; that is, two-phase systems including IL as one of the phases can be stable. A number of the separated systems are known in which the IL dissolves only catalyst, whereas the nonionic liquid dissolves the corresponding substrate. It appeared that such systems are very useful in application to heterogeneous catalysis:⁷ reaction between the substrate and the catalyst occurs when the substrate diffuses through the phase boundary into the IL. It seems plausible that the higher the area is of the interface between the ionic and nonionic liquids, the more efficient is the catalytic system. Since the microscopically segregated state of the mixture is one of those that possesses a high interfacial area, determination of the conditions of its stability is of interest.

The possibility of microphase separation in a pure IL⁹ and in a mixture of the IL with nonionic solute¹⁰ has been predicted by means of computer simulations. In these articles, the structure

of the ions of IL and of the solute was explicitly taken into account. It has been shown that the ions, consisting of polar and nonpolar parts are ordered in such a way that the polar and nonpolar domains are formed. Microscopically segregated two-component systems comprising an IL as one of the components were also reported in experimental works. The examples are IL aggregates formed in an aqueous solution²⁴ and clathrate structures found in IL–benzene mixtures.^{25,26}

Instability of the macroscopic phase separation of the ionic and nonionic liquids toward microphase segregation was demonstrated in our recent publication.¹⁴ Here a Flory–Huggins type theory was developed to calculate the structure of the interfacial layer and the surface tension coefficient. We have shown that, if affinities of the cations and the anions to the neutral molecules differ significantly, the surface tension of the interface can be negative. It implies that the structure of a high interfacial area (microstructure) is more stable than the coexisting macrophases.

In order to support the results of ref 14, in the present paper, we analyze an opposite (compared to ref 14) regime of the mixture (i.e., conditions of instability of the homogeneous state of the mixture toward microphase separation). This (the so-called weak segregation) regime allows the spatial length scale (the wave vector) of weak concentrations modulations near the critical point to be calculated. In our consideration, we combine the Flory–Huggins type approach^{13,14,20,21} and the random phase approximation that is commonly used for the theoretical study of microphase separation in various polymer systems.^{16–19}

The Model

The mixture of ionic and nonionic liquids is treated as a “three-component” system including anions, cations, and neutral molecules. Each ion is considered to consist of a charged group surrounded by a neutral “bulky” shell. The shells of the ions interact with each other and with the neutral molecules via short-range forces.^{13,14} It makes this approach distinct from the one used in refs 11 and 12. For the sake of simplicity, it is assumed that the sizes of the ions and of the neutral molecules are the same.

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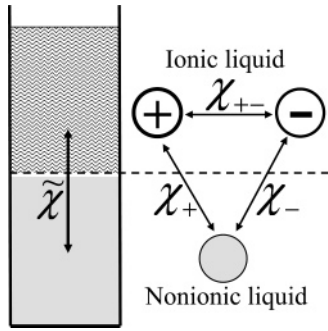


Figure 1. Schematic diagram describing the interaction parameters used in the paper.

Since we analyze microphase separation, it should be taken into account that the volume fractions of the cations and anions, $\Phi_+(\mathbf{r}), \Phi_-(\mathbf{r})$, depend on the spatial coordinate \mathbf{r} and that they are generally not equal to each other in every point of the system, $\Phi_+(\mathbf{r}) \neq \Phi_-(\mathbf{r})$. In other words, a violation of the local electric neutrality of the microscopically separated mixture is possible, whereas the mixture is neutral as a whole, $\int_V \Phi_-(\mathbf{r}) d\mathbf{r} = \int_V \Phi_+(\mathbf{r}) d\mathbf{r}$. Here $\int_V d\mathbf{r}$ denotes integration over the whole volume of the system, V . The total free energy functional of the mixture can be expressed as a sum of two contributions

$$F_{\text{tot}} = F_{\text{FH}} + E_{\text{el-st}} \quad (1)$$

The first term is a generalization of the Flory–Huggins free energy of a three-component mixture for the case of spatially inhomogeneous distribution of the components^{14,15}

$$F_{\text{FH}} a^3 / k_B T = \int_V d\mathbf{r} \left\{ \Phi_+(\mathbf{r}) \ln \Phi_+(\mathbf{r}) + \Phi_-(\mathbf{r}) \ln \Phi_-(\mathbf{r}) + \Phi_s(\mathbf{r}) \ln \Phi_s(\mathbf{r}) + \chi_{+-} \Phi_+(\mathbf{r}) \Phi_-(\mathbf{r}) + \chi_+ \Phi_+(\mathbf{r}) \Phi_s(\mathbf{r}) + \chi_- \Phi_-(\mathbf{r}) \Phi_s(\mathbf{r}) + \frac{a^2}{6} [\chi_+ (\nabla \Phi_+)^2 + \chi_- (\nabla \Phi_-)^2 + (\chi_+ + \chi_- - \chi_{+-}) \nabla \Phi_+ \nabla \Phi_-] \right\} + \text{const} \quad (2)$$

Here $\Phi_s(\mathbf{r})$ is the volume fraction of the neutral molecules that is determined by an incompressibility condition, $\Phi_s(\mathbf{r}) = 1 - \Phi_+(\mathbf{r}) - \Phi_-(\mathbf{r})$, and a is the size of the elementary cell so that the volume of the cell (the excluded volume of the molecule/ion) is equal to a^3 . The first three terms of eq 2 represent the entropy of the translational motion of the cations, the anions, and the neutral molecules, respectively. The next three terms of eq 2 are responsible for the volume interactions of the ions with each other, of the cations with the neutral molecules, and of the anions with the neutral molecules. χ_{+-} , χ_+ , and χ_- are the corresponding Flory–Huggins parameters, Figure 1. The gradient terms in the square brackets of eq 2 are the free energy losses because of inhomogeneous distribution of the components. A rigorous derivation of these terms can be found in refs 14 and 15.

The second term of eq 1 is the energy of the electrostatic field in the inhomogeneous mixture

$$E_{\text{el-st}} = \frac{1}{2} \int_V d\mathbf{r} \rho(\mathbf{r}) \varphi(\mathbf{r}) \quad (3)$$

Here $\rho(\mathbf{r})$ and $\varphi(\mathbf{r})$ are the charge density of the mixture and the potential of the electrostatic field, respectively. These two functions are connected via the Poisson equation

$$\Delta \varphi(\mathbf{r}) = -4\pi \frac{\rho(\mathbf{r})}{\epsilon} \quad (4)$$

where ϵ is the average dielectric constant of the homogeneous mixture. The charge density $\rho(\mathbf{r})$ is determined by the difference of the concentrations of the cations and anions

$$\rho(\mathbf{r}) = e \frac{\Phi_+(\mathbf{r}) - \Phi_-(\mathbf{r})}{a^3} \quad (5)$$

where e is the absolute value of the charge of the ion. Definitely, if the concentrations profiles of the cations and anions coincide, $\Phi_+(\mathbf{r}) = \Phi_-(\mathbf{r})$, or if the mixture is homogeneous, $\Phi_+(\mathbf{r}) = \Phi/2$, $\Phi_-(\mathbf{r}) = \Phi/2$ (the constant Φ is the total volume fraction of the ions in homogeneous mixture), the charge density is equal to zero.

The main objective of this work is to determine the instability condition of the homogeneous mixture toward microscopic phase separation. To do so, let us consider small harmonic concentrations modulations

$$\Phi_+(\mathbf{r}) = \Phi/2 + \delta\Phi_+(\mathbf{r}) = \Phi/2 + A_+ \cos(\mathbf{q}^* \cdot \mathbf{r}), A_+, A_- \ll \Phi$$

$$\Phi_-(\mathbf{r}) = \Phi/2 + \delta\Phi_-(\mathbf{r}) = \Phi/2 + A_- \cos(\mathbf{q}^* \cdot \mathbf{r}) \quad (6)$$

and check whether these modulations increase or decrease the free energy of the homogeneous state of the mixture. The decreasing would mean that the homogeneous state becomes unstable. In eq 6, the wave vector \mathbf{q}^* characterizes the length scale D (periodicity) of the modulations, $D = 2\pi/q^*$, $q^* = |\mathbf{q}^*|$. Substitution of eq 6 into eq 1 and expansion of the logarithmic terms into a series in powers of A_{\pm} (up to the second power) allows the total free energy to be represented in the form

$$F_{\text{tot}} = F_h + \delta F, |F_h| \gg |\delta F| \quad (7)$$

where F_h is the free energy of the homogeneous mixture^{13,14}

$$\frac{F_h a^3}{k_B T V} = \Phi \ln(\Phi/2) + (1 - \Phi) \ln(1 - \Phi) + \chi_{+-} \frac{\Phi^2}{4} + \chi \Phi (1 - \Phi) \quad (8)$$

and correction δF is due to the concentrations modulations

$$\begin{aligned} \frac{\delta F a^3}{k_B T V} = & \frac{A_+^2}{2} \left(\frac{1}{\Phi} + \frac{1}{2(1 - \Phi)} - (\chi + \Delta\chi) \left(1 - \frac{\tilde{q}^2}{6} \right) + \frac{\tilde{l}}{2\tilde{q}^2} \right) + \\ & \frac{A_-^2}{2} \left(\frac{1}{\Phi} + \frac{1}{2(1 - \Phi)} - (\chi - \Delta\chi) \left(1 - \frac{\tilde{q}^2}{6} \right) + \frac{\tilde{l}}{2\tilde{q}^2} \right) + \frac{A_+ A_-}{2} \\ & \left(\frac{1}{1 - \Phi} - (2\chi - \chi_{+-}) \left(1 - \frac{\tilde{q}^2}{6} \right) - \frac{\tilde{l}}{\tilde{q}^2} \right) \quad (9) \end{aligned}$$

Here \tilde{q} is the dimensionless value of the wave vector of the modulations, $\tilde{q} = a q^*$, and dimensionless parameter $\tilde{l} = 4\pi e^2 / \epsilon a k_B T$ is a measure of the strength of the electrostatic interactions with respect to the energy of the thermal motion (the ratio of the Bjerrum length to the size of the molecule). In addition, we introduced new parameters

$$\begin{aligned} \chi &= \frac{(\chi_+ + \chi_-)}{2} \\ \Delta\chi &= \frac{(\chi_+ - \chi_-)}{2} \end{aligned} \quad (10)$$

The first one has a meaning of the “average” affinity of the ionic to nonionic liquid, whereas the second parameter characterizes the difference of the affinities of cations and anions to the neutral molecules.

Obviously, the amplitudes of the small modulations, A_+ , A_- , are dependent on each other: excitation of the cations concentration will cause excitation of the anions concentration. Relation between the amplitudes can be found from the condition of the thermodynamic equilibrium. Minimization of δF over A_- results in

$$\frac{\delta F a^3}{k_B T V} = G \frac{A_+^2}{2} \quad (11)$$

$$G = -\chi - \Delta\chi + \frac{1}{\Phi} + \frac{1}{2(1-\Phi)} + \frac{\tilde{q}^2}{6}(\chi + \Delta\chi) + \frac{\tilde{l}}{2\tilde{q}^2} - \frac{1}{4} \frac{\left(\chi_{+-} - 2\chi + \frac{1}{(1-\Phi)} + \frac{\tilde{q}^2}{6}(-\chi_{+-} + 2\chi) - \frac{\tilde{l}}{\tilde{q}^2}\right)^2}{-\chi + \Delta\chi + \frac{1}{\Phi} + \frac{1}{2(1-\Phi)} + \frac{\tilde{q}^2}{6}(\chi - \Delta\chi) + \frac{\tilde{l}}{2\tilde{q}^2}}$$

If G is positive at all values of \tilde{q} , the free energy of any disturbed state is more than that of the homogeneous state, and microphase separation is impossible. As soon as G reaches zero at some value of \tilde{q}^* (corresponding to the minimum of G as a function of \tilde{q}) and then becomes negative, the homogeneous state is no more stable and microstructure with the period $2\pi a/\tilde{q}^*$ is favorable. Therefore, the boundary of the stability of the homogeneous mixture (the spinodal of microphase separation) is determined by equations

$$G = 0 \quad \partial G / \partial \tilde{q} = 0 \quad (12)$$

It has to be noted that solutions of eq 12 can exist not only at $\tilde{q} \neq 0$, but also at $\tilde{q} = 0$. The latter corresponds to the spinodal of the macroscopic phase separation.

Results and Discussion

Before analyzing eq 12, it is necessary to note that below we will consider only regimes of large scale concentrations modulations, $D \gg a$ (i.e., $\tilde{q} \ll 0$). There are two reasons for that. First, the derivation of the gradient terms of eq 2 assumes gradual variations of the concentrations profiles. It means that the characteristic length scale of the variations has to be much larger than the size of the molecules; that is, inequality $D \gg a$ has to be fulfilled. Second, in our model, we use very strong simplification comprising equality of the sizes and shapes of all units of the systems. One can expect that if the period of the microstructure is comparable with the size of the molecules the molecular shape and size should play a dominant role in formation of the shape and symmetry of microdomains. However, if the domain size exceeds significantly the size of the molecules (i.e., the microstructure is stabilized by the long range (in our case Coulomb) interactions), the role of the shape and the size of the ions/molecules is diminished, and our approximation of the single microscopic size becomes quite accurate.

Thus, keeping in mind that $\tilde{q} \ll 0$, we can expand G , eq 11, into a series in powers of \tilde{q}^2

$$G \approx G_0 + B\tilde{q}^2 + C\tilde{q}^4 \quad (13)$$

where

$$G_0 = \frac{2}{\Phi(1-\Phi)} - 4\tilde{\chi}$$

$$B = \frac{2}{3}\tilde{\chi} - \frac{(G_0 + 2\Delta\chi)^2}{2\tilde{l}}$$

$$C = \left(\frac{1}{2\Phi} + \frac{G_0 - \chi_{+-}}{4} + \Delta\chi\right) \frac{(G_0 + 2\Delta\chi)^2}{\tilde{l}^2} - \frac{(G_0 + 2\Delta\chi)(2\tilde{\chi} - \Delta\chi)}{3\tilde{l}} \quad (14)$$

and we introduce $\tilde{\chi} = \chi - \chi_{+-}/4$. The physical meaning of this parameter was discussed in ref 13: it characterizes a solvent power of the IL. For the sake of simplicity, we will set $\chi_{+-} = 0$ in our further calculations; that is, $\tilde{\chi}$ will also be related to the affinity of the ionic to nonionic liquid.

If the interaction parameters of the system correspond to the case $B > 0$, then the last term of eq 13 is negligible and G has a minimum at $\tilde{q} = 0$. It means that the macroscopic phase separation occurs and eq 12 for the spinodal has the form $G_0 = 0$. In the case of the negative value of the coefficient B , $B < 0$, G has the minimum at nonzero value of the wave vector

$$(\tilde{q}^*)^2 = -\frac{B}{2C} \ll 1 \quad (15)$$

and equation for the spinodal of the microphase separation takes the form

$$G_0 - \frac{B^2}{4C} = 0 \quad (16)$$

Merging of the spinodals of the macro- and microphase separation occurs at the Lifshitz point²² that is determined by the conditions $G_0 = 0$ and $B = 0$

$$\tilde{\chi} = \frac{3\Delta\chi^2}{\tilde{l}} \quad (17)$$

Thus, if the anions and cations have identical χ parameters for interactions with the neutral molecules, $\Delta\chi = 0$, then the Lifshitz point does not exist and the macroscopic phase separation occurs (at least at $\chi_{+-} = 0$). In the Lifshitz point, the parameter C is positive and nonvanishing, $C = 2\Delta\chi^2/(3\tilde{l})(1 + 3/\tilde{l}\Phi) > 0$ ($\chi_{+-} = 0$); therefore, near this point, the condition $\tilde{q}^* \ll 1$ is fulfilled.

The spinodal of the mixture is plotted in Figure 2 in the coordinates Φ – $\tilde{\chi}$ at fixed values of the parameters $\Delta\chi$, χ_{+-} , and \tilde{l} . Curves a and b differ by a value of the parameter $\Delta\chi$, $\Delta\chi = 3$ (a) and 2.7 (b). Below each of the curves, the homogeneous mixture is stable. The $\tilde{\chi}$ coordinate of the Lifshitz point is determined by eq 17, and the Φ coordinates are calculated using eq 17 and $G_0 = 0$: $\Phi(1-\Phi) = \tilde{l}/6\Delta\chi^2$. Due to the symmetry with respect to the substitution of Φ by $1-\Phi$, there are two Lifshitz points in the Φ – $\tilde{\chi}$ coordinates: P_1 , P_2 (a), and M_1 , M_2 (b). Between these points, i.e., at $\Phi_{P_1} < \Phi < \Phi_{P_2}$ or $\Phi_{M_1} < \Phi < \Phi_{M_2}$, the spinodal corresponds to the instability at nonzero wave vector, and for the region above this segment of the $\tilde{\chi}(\Phi)$ curve, the microphase separation occurs. Outside the segment,

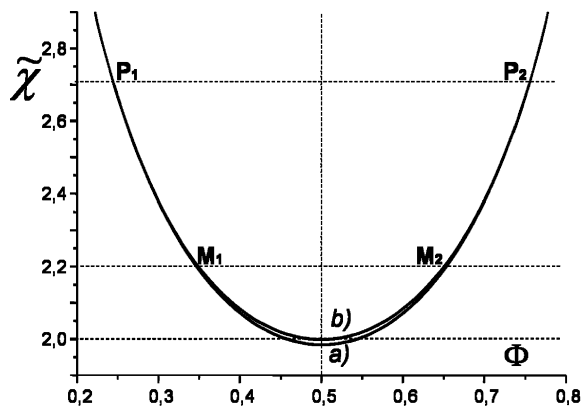


Figure 2. Spinodal of microphase separation in the mixture of ionic and nonionic liquids for $\tilde{l} = 10$, $\chi_{+-} = 0$, $\Delta\chi = 3$, (a), and $\Delta\chi = 2.7$ (b). P_1, P_2 and M_1, M_2 are the Lifshitz points for cases a and b, respectively.

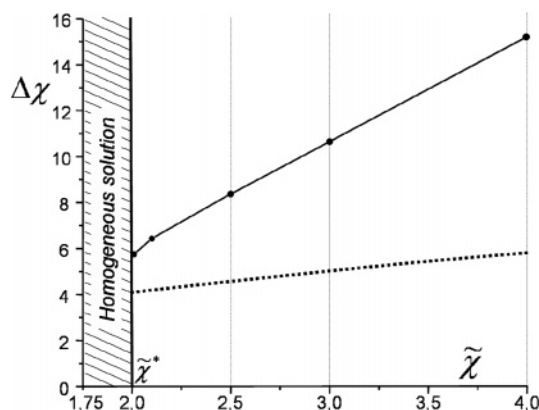


Figure 3. Schematic phase diagram of the mixture of ionic and nonionic liquids (solid lines) obtained in ref 14. Dotted line, eq 17, is a boundary between microscopic and macroscopic phases.

i.e., at $\Phi \leq \Phi_{P_1}$ and $\Phi \geq \Phi_{P_2}$ or at $\Phi \leq \Phi_{M_1}$ and $\Phi \geq \Phi_{M_2}$, the spinodal corresponds to the macroscopic phase separation. One can see from Figure 2 that the higher $\Delta\chi$ is, the wider a “window” of the transition to the microphase is. This effect has a clear physical meaning. The parameter $\Delta\chi$ characterizes the difference in affinities of the cations and anions to the neutral molecules. Therefore, the higher the difference is, the higher the tendency to local segregation of the cations and anions is (i.e., to the formation of the locally electrically charged system).¹⁴ Keeping in mind that the electrostatic interactions are responsible for stabilization of microphases,²³ we can conclude that the increase of the strength of the local electric field with $\Delta\chi$ widens the range of values of other parameters corresponding to the microphase separation.

The obtained results are in qualitative agreement with our recent predictions for the instability of macroscopic phases.¹⁴ We have shown that the surface tension coefficient of coexisting ionic and nonionic liquids can become negative with the increase of $\Delta\chi$.¹⁴ It implies that the structure having a high interfacial area (microstructure) is more stable than the coexisting macrophases. The schematic phase diagram of ref 14, obtained for the fraction of the ionic liquid $\Phi = 1/2$ and $\tilde{l} = 8\pi$, is presented in Figure 3. The solid line with dots corresponds to the condition of equality of the surface tension coefficient to zero. Above and below this curve, the micro- and macrostructures are stable, respectively. The vertical line is a boundary of the homogeneous phase that shifts to the right-hand side with variation of Φ . If we plot in this diagram the $\Delta\chi$ – $\tilde{\chi}$ dependence at the Lifshitz

point (dotted line), eq 17, we also find that the microphase can be stable only above this line (i.e., with the increase of $\Delta\chi$).

Formally, our theory predicts the microphase separation in pure ionic liquids as well. In this case, the function G has a very simple form

$$G = 2 - \chi_{+-} + \chi_{+-} \frac{\tilde{q}^2}{6} + \frac{2\tilde{l}}{\tilde{q}^2} \quad (18)$$

and the physical reason for the separation is a competition between (i) the short-range demixing of the shells of the cations and anions ($\chi_{+-} \neq 0$) and (ii) the long-range Coulomb forces (note that the macroscopic phase separation is suppressed in this system). Equation 12 takes the form

$$(\tilde{q}^*)^2 = \sqrt{\frac{12\tilde{l}}{\chi_{+-}}} \quad 2 - \chi_{+-} + 2\sqrt{\frac{\tilde{l}\chi_{+-}}{3}} = 0 \quad (19)$$

that have solutions $\tilde{q}^*, \chi_{+-} \sim 1$ at $\tilde{l} \sim 1$. As we mentioned above, in this regime, the gradient terms of eq 2 have to be corrected, and the size and shape of the ions start to play an important role. The solution of eq 19 is quantitatively correct, if $\tilde{l} \ll 1$. It corresponds to the case of ions with very large shells. The microphase separation of an IL was also predicted in ref 9 by means of computer simulations where peculiarities of the internal structure of cations and anions were taken into account.

Conclusions

We developed a theory of microphase separation in a mixture of ionic and nonionic liquids. Each ion of the IL was modeled by a charge surrounded by a neutral shell. The shells of the cations and the anions were considered to have different affinities to the neutral molecules. The different affinities lead to the segregation of the cations and anions. However, due to the presence of the charge units, they cannot segregate macroscopically, and violation of the electric neutrality (formation of the electric field) occurs only at the finite length scales. Competing short-range demixing and long-range Coulomb interactions result in the formation of the microstructure (i.e., alternating IL-rich and IL-poor regions). The characteristic length scale of the density modulations depends on the difference in the affinities: the lower the difference is, the larger the inhomogeneities are. It has to be noted that the analysis of the spinodal of microphase separation done in our paper does not allow a shape of the domains and symmetry of their spatial organization to be predicted. To do so, a Landau type theory of phase transitions¹⁷ (for the so-called weak segregation regime) or the strong segregation theory²³ have to be developed. The latter will be reported in a forthcoming publication.

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