

“Amphiphilic” Ionic Liquid in a Mixture of Nonionic Liquids: Theoretical Study

Artem A. Aerov,* Alexei R. Khokhlov, and Igor I. Potemkin

Physics Department, Moscow State University, Moscow 119992, Russian Federation, and
Department of Polymer Science, University of Ulm, 89069 Ulm, Germany

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We use a Flory–Huggins type approach to describe a two-phase system consisting of nonionic components A and B that are incompatible with each other and of an ionic liquid (IL). The anions and the cations of the IL are considered as independent components and are assumed to have different affinities for A and B. We show that an up to several hundreds molecules thick double electrostatic layer is formed by the IL at the phase boundary, and the surface tension of the boundary happens to be smaller in the case of the three-component system than in the case of a two-component system consisting of the components A and B only; i.e., the IL plays the role of a surfactant. We investigate by means of a numerical calculation the full range of possible IL concentrations in the bulk of the two phases and also consider analytically the case of the low IL concentrations. The results obtained by means of the two methods are in perfect agreement.

Introduction

In the last 10 years, ionic liquids (ILs) strongly have attracted the interest of researchers because it was found that these substances possess some unique and very useful properties. ILs are solely composed of anions and cations. Nevertheless, they are liquid at around room temperature.^{1,2} The main advantageous peculiarity of ILs is the fact that they are very good as solvents and reaction media. This is because ILs are almost nonvolatile^{3–5} and at the same time they can dissolve a wide range of both organic and inorganic substances.^{1,6,7} For example, an important achievement related to the high solvent power of ILs is the invention of the novel effective and environmentally friendly cellulose processing technique.⁸

The list of promising applications of ILs is really long. What one has to mention is the possibility of producing almost an infinite number of different ILs by means of combining different cations with different anions.^{1,9} It is thus possible to carry out the search of an IL with desired predefined properties.

Chemical structures of different ILs can differ significantly from each other. Of course, properties of an individual IL are explained by its chemical structure. But at the same time, it is evident that the useful properties of ILs are somehow generally inherent to ILs nature; i.e., there are some physical laws or mechanisms that are valid for ILs as a *whole class* of substances. (There is to be something more than just the name that unifies ILs.) One of the main goals of researchers is to reveal these laws.

It is evident that general properties of ILs are to be somehow related to the main basic feature of ILs: ILs are composed of ions only. An interesting concept can be drawn from the latter simple fact. Namely, an IL can have a unique dual nature that can be the reason for many interesting properties that are unusual for common liquids. The concept of ILs dual nature now becomes more and more popular.¹⁰ The reason for the dual nature lies in the fact that the properties of the IL's cations can strongly differ from the properties of the IL's anions. The contradictory properties of the two types of particles would

immediately make them segregate if (just hypothetically!) the electrostatic interactions vanished. But the coulomb attraction makes these “incompatible” particles stay together in an intermixed state and compose thus a substance (the IL), with unusual dual nature.

On the basis of this concept, we have already explained and predicted theoretically several phenomena related to ILs. We have shown that the high solvent power of an IL may be caused by the high energy of the short-range (i.e., noncoulomb) interactions of its cations with its anions.¹¹ Later¹² we have shown that a double electrical layer that appears at the boundary of an IL and a nonionic liquid¹³ may be caused by the difference in the affinities of the IL's cations and the IL's anions to the nonionic liquid molecules. We have also demonstrated^{12,14} that the microheterogeneous structures^{15,16} that can be observed in the mixture of an IL and a nonionic liquid may be caused by the high difference of these affinities. In a subsequent publication¹⁷ we extended the idea and predicted that the difference in affinities of an IL's cations and anions to a polymer gel with immobilized carbon nanotubes can lead to the situation when the swelling ratio of the gel particle depends on its size.

Another interesting phenomenon that can be related to the dual nature of ILs is the bending in electric field of a thin film of polymer gel impregnated with an IL.¹⁸ In this case the duality of the IL lies in the difference of its cations and its anions sizes. If electric field is applied, the larger (smaller) cations go to one side of the film and the smaller (larger) anions go to the other side, which makes the film bend.

In the present paper we use an approach based on the lattice model that was used in our previous papers^{11,12,14,17} to analyze the properties of the system consisting of an IL and of two types of nonionic molecules, A and B. This time we suppose that the duality of the IL shows up in different affinities of the IL's cations and the IL's anions to A and to B: the cations are attracted stronger to A than to B and anions *vice versa* are stronger attracted to B than to A.

We consider a two-phase system in which the two phases are formed because the nonionic components A and B are incompatible with each other (they cannot form a homogeneous mixture), and the affinities of the IL as a whole (of the cation

* To whom correspondence should be addressed. E-mail: aerov@polly.phys.msu.ru.

and the anion taken together) to the both phases are same. We investigate how the ions of the IL are distributed near the phase boundary and how the IL contributes to the value of the phase boundary surface tension.

Distribution of an ionic admixture at an interface and the influence of the admixture on the surface tension has been already rather extensively investigated. It was known already about hundred years ago that an ionic admixture increases surface tension.¹⁹ The experimental work²⁰ is one of the recent ones devoted to this subject. The phenomenon has been attracting the interest of researchers for already a long time, since there is a much better known opposite phenomenon of the surface tension decrease by addition of a surfactant.

One of the first theoretical works on the subject was published in 1934 by Onsager and Samaras.²¹ A phase boundary between a gas and a liquid containing an ionic admixture has been considered therein. The Onsager–Samaras (OS) theory is based on the Debye–Hückel approach and on the assumption that an ion induces charge on the phase boundary. The induced charged repels the ion. This leads to the decrease of the ions concentration near the boundary (as compared to the bulk liquid) and to the increase of the surface tension. The OS model has been further developed¹⁹ by means of taking into account that the solvate shells of ions do not allow them to approach the phase boundary closer than the size of the shell, which makes the effect more pronounced. The theory has been also generalized²² for the case of an electrolyte a cation of which carries several times smaller or larger charge than an anion. Another generalization of the OS theory²³ is supposing that polarizability of cations differs from the polarizability of anions. The ability of an ion to be polarized originates an additive to its potential in the field produced by the charge induced on the phase boundary by the very ion. Such a break in the symmetry of the oppositely charged ions leads to the inequality of their concentrations near the phase boundary, i.e., an electrostatic double layer arises.

The aforementioned theoretical works^{19,21–23} are based on the Debye–Hückel approach; i.e., only small concentrations of ions are considered therein. A straightforward way to allow for also high concentrations of ions is to do a computer simulation. This has been done in the work,²⁴ in which a Monte Carlo simulation of an entire liquid drop has been carried out. It should be also mentioned that these works consider only the so-called²⁵ *Coulombic* electrolyte systems, i.e., the systems behavior of which is driven only by electrostatic interactions. (The short-range van der Waals forces are not taken into account). Generally, real electrolyte systems are *solvophobic*; i.e., their behavior is determined not only by electrostatic interactions but also by mutual affinities of their components molecules.

A *solvophobic*²⁵ two-phase mixture is considered theoretically in the work.²⁶ It is analyzed therein how electrolyte is distributed at a phase boundary of two nonionic substances and how that influences the surface tension of the boundary. It is taken into account that cations and anions have different affinities for the two phases and that ions are affected by charge induced in the medium on the inhomogeneities of the dielectric constant. The calculations are based on the Ginzburg–Landau theory and are valid for low concentrations of ions and for a system that is close to the critical point.

In the present work we take into account in almost the simplest way only the main factors, which are the entropy, the electrostatic field, and the van der Waals interactions of the components, and ignore image potential, polarizability of ions, ion pairing, fluctuations, etc. (the ignored factors are less important in the considered case). This allows us to build a

transparent theory that is not overloaded with details that confuse the one who tries to comprehend calculation results and understand the role of the factors taken into account. And the main advantage of our approach lies in the fact that it does not require vicinity of the critical point or low concentrations of ions. So, it is applicable not only to electrolyte solutions but also to mixtures comprising ILs (i.e., mixtures in which the volume fraction of ions is on the order of unity).

Method

The Flory–Huggins like lattice model is used. It is supposed that ions and molecules A and B are of the same size and each of them occupies a cell of a cubic lattice. The cells have the size a . All of them are occupied. The anions and the cations of the IL are treated as individual “components” that move independently. Thus our approach is different from the one used in the works^{27,28} where cation and anion of an IL are treated as a single molecular entity.

In fact, some cations and anions form ion pairs that move as single molecular entities, and the concentration of free charges decreases for this reason. However, this effect would not change qualitatively the phenomenon predicted by our theory. That is why we do not take it into account in order not to overload our consideration with minor details. Besides, this decrease of separately moving ions concentration can be effectively modeled in the framework of our theory by means of varying the value of the ions volume fraction $\phi_{\text{ions}}^{\infty}$ far from the boundary (see below).

We also do not take into account fluctuations of ion concentrations. This effect is minor at small concentrations of the ions because the energy of attractive interactions between the ions in the Debye–Hückel approximation is known to be negligible in comparison with the energy of thermal motion.²⁹ At high concentrations of ions the electrostatic forces are short-range and they can be taken into account within the lattice theory we use by means of renormalizing the interaction parameters.

One more minor effect we neglect is the image potential that appears due to the charge induced in the dielectric medium at the phase boundary. But this charge appears if there are inhomogeneities of dielectric constant in the considered system. Thus we just assume that dielectric constants of all the components comprising the considered system are the same and so the dielectric constant of their mixture does not depend on the mixture’s composition. The polarization of ions²³ is also not to be considered then.

Let us consider the two-phase system as a sequence of flat elementary layers parallel to the phase boundary. Each of them is composed of elementary cubic cells and is one cell thick. Let us denote as ϕ_+^i , ϕ_-^i , ϕ_A^i , ϕ_B^i the volume fractions of respectively cations, anions, molecules A, and molecules B in the i th layer. Let us denote the potential of electrostatic field in the center of the i th layer as φ^i . Let us introduce the dimensionless potential $\tilde{\varphi}^i = \varphi^i(e/kT)$, where e is the elementary charge (in the model the cations and the anions carry the charge of the same absolute value), k is the Boltzmann constant, and T is the absolute temperature of the system. One can write then the free energy F of the system per unit area of the phase boundary as

$$F \frac{a^2}{kT} = \sum_i (\phi_+^i \ln \phi_+^i + \phi_-^i \ln \phi_-^i + \phi_A^i \ln \phi_A^i + \phi_B^i \ln \phi_B^i) + \frac{1}{2} \sum_i \tilde{\varphi}^i (\phi_+^i - \phi_-^i) + F_{\text{contacts}} \quad (1)$$

The first term in the right part of eq 1 is the entropic part of the free energy. The second term represents the energy of electrostatic field. The last term represents the total energy of the components molecules contacts (van der Waals interactions). It can be written as

$$F_{\text{contacts}} = \frac{1}{2} \sum_i \sum_{p,q} \phi_p^i \phi_q^i \chi_{pq} + \sum_i a^2 \sigma_{i(i+1)} \quad (2)$$

where each of the indexes p and q denotes one of the components (+, −, A, or B), χ_{pq} is the Flory–Huggins parameter that characterizes the van der Waals interactions of the component p with the component q , and $\sigma_{i(i+1)}$ is the normalized to kT surface energy of the contact of the i th and the $(i+1)$ th elementary layers. It should be stressed that the parameter χ_{+-} has nothing to do with Coulomb interactions. Of course, the discrimination of the “in-layer bulk” and “interlayer surface” components of this free energy part is just symbolic in the considered case.

One can find in the first appendix of our paper¹⁷ the derivation of the formula:

$$\sigma_{i(i+1)} = \frac{1}{6a^2} \sum_p \sum_q \chi_{pq} \left(\phi_p^i \phi_q^{i+1} - \frac{1}{2} \phi_q^i \phi_q^i - \frac{1}{2} \phi_p^{i+1} \phi_p^{i+1} \right) \quad (3)$$

If gradients of the mixture components concentrations vary in space slowly, one can use the approximate formula

$$\frac{\phi_p^{i+1} + \phi_p^{i-1} - 2\phi_p^i}{a^2} = \frac{\partial^2 \phi_p(z)}{\partial z^2} \quad (4)$$

(where the coordinate z is perpendicular to the phase boundary) to transform eq 3 and the whole expression (1) to the continuum limit. This is explained in detail in the appendix of our paper¹² or in the textbook.³⁰

Anyway, as it turns out, the transformation to the continuous limit is not necessary for the numerical calculation and can even cause some technical problems. So there is no need also in using the assumption in (4), which would impose extra limitations on the worked out theory.

If one substitutes the eq 3 into the eq 2, one gets

$$F_{\text{contacts}} = \frac{1}{3} \sum_i \sum_{p,q} \phi_p^i \phi_q^i \chi_{pq} + \frac{1}{6} \sum_i \sum_{p,q} \phi_p^i \phi_q^{i+1} \chi_{pq} \quad (5)$$

It should be noted that $\chi_{pp} \equiv 0$ (see appendix of the work¹²).

It follows from the boundary conditions for electrostatic field that

$$\tilde{\varphi}^{i+1} + \tilde{\varphi}^{i-1} - 2\tilde{\varphi}^i = -4\pi u (\phi_+^i - \phi_-^i) \quad (6)$$

where $u = e^2/kT\epsilon a$, and ϵ is the dielectric constant of the medium. We suppose for simplicity that ϵ is equal to a constant in all the points of the considered mixture. In the continuous limit the eq 6 turns into the Poisson equation.

Since each elementary cell of the lattice is occupied by one molecule of a component the following condition must be fulfilled:

$$\phi_+^i + \phi_-^i + \phi_A^i + \phi_B^i = 1 \quad (7)$$

Chemical potential μ_p of each component p in all the layers is the same:

$$\frac{\delta F}{\delta \phi_p^i} = \mu_p \quad (8)$$

To determine the chemical potentials μ_p , one can apply eq 8 for layers that are far from the boundary in the bulk of the two phases. (Concentrations of the components there can be determined from the binodal conditions.) It should be noted that the chemical potentials μ_- and μ_+ are determined up to a constant together with the electrostatic potential. For example, as soon as the electrostatic potential at $z = -\infty$ is determined (e.g., $\tilde{\varphi}(-\infty) = 0$) one can calculate μ_- and μ_+ using eq 8 if the concentrations of the components at $z = -\infty$ (in the bulk of one of the phases) are known. After that, one can calculate $\tilde{\varphi}(+\infty)$ using again eq 8 if one knows the concentrations of the components in the other phase. Thus, the difference of the electrostatic potentials in the bulks of the two phases (the so-called Galvani potential difference²⁶) is determined by the concentrations of the components in the two phases and does not depend on the concentration profiles at the phase boundary.

We use eq 7 to exclude the variables ϕ_B^i and then minimize numerically the free energy of the system, i.e., determine the concentrations of the components and the electrostatic potentials in all the elementary layers at the phase boundary that satisfy eqs 6 and 8.

As soon as the concentrations and the electrostatic potential profiles near the phase boundary are determined, one can calculate the phase boundary surface tension. The surface energy is the difference between the free energy of the interface transition layer and the free energy the two phases would acquire if the substance constituting the transition layer were absorbed by them. If some molecules are added to a phase, both the corresponding concentrations in the phase and the volume of the phase are increased slightly. The corresponding contributions to the phase free energy are determined by the chemical potentials of the molecules and by the osmotic pressure in the phase. Of course, free energies of the two phases which are in equilibrium are increased by same values if same amounts of same molecules are added to them. So we determined the surface tension γ of the phase boundary by the formula

$$\frac{\gamma a^2}{kT} = \frac{F a^2}{kT} - I \left(f - \phi_A \frac{\partial f}{\partial \phi_A} - \phi_{\text{ions}} \frac{\partial f}{\partial \phi_{\text{ions}}} \right) \Big|_{z=-\infty} - \sum_i \left(\frac{\partial f}{\partial \phi_A} \Big|_{-\infty} \phi_A^i + \frac{\partial f}{\partial \phi_{\text{ions}}} \Big|_{z=-\infty} (\phi_+^i + \phi_-^i) \right) \quad (9)$$

In (9) I is the number elementary layers composing the interface transition layer, i.e., the number of different values of the index i . Strictly speaking, the interface transition layer extends infinitely far in the bulks of the two phases and F and I are infinitely large. But to carry out the numerical calculation with a certain accuracy one can treat a finite I .

In eq 9 f is the normalized to kT free energy per elementary cell in the bulk of one of the two phases, i.e., far from the interface (it does not matter which of the two phases: the one we denote as $z = -\infty$ or the one we denote as $z = +\infty$):

$$f = \phi_{\text{ions}} \ln \phi_{\text{ions}} + \phi_A \ln \phi_A + (1 - \phi_A - \phi_{\text{ions}}) \times \ln(1 - \phi_A - \phi_{\text{ions}}) + \chi_{AB} \phi_A (1 - \phi_A - \phi_{\text{ions}}) + \frac{1}{2} \phi_{\text{ions}} (\chi_{+A} + \chi_{-A}) \phi_A + \frac{1}{2} \phi_{\text{ions}} (\chi_{+B} + \chi_{-B}) (1 - \phi_A - \phi_{\text{ions}}) \quad (10)$$

where ϕ_{ions} is the volume fraction of ions (in the considered case, volume fractions of the cations and the anions are equal to each other far from the interface; we assume also for definiteness that $\chi_{+-} = 0$) and ϕ_A is the volume fraction of A molecules. It should be noted that in the phase boundary transition layer the total amount of cations is equal to the total amount of anions. Otherwise, the energy of electrostatic field would be infinitely large. So, one does not need to write separately the volume fractions of cations and anions in the eq 10 to determine the increase of a phase bulk free energy caused by the “absorption” of the substance composing the phase boundary transition layer. Equation 10 can be derived from eqs 1, 5, and 7. The functional $f(\phi_{\text{ions}}, \phi_A)$ described by eq 10 determines also the composition of the two phases.

Results and Discussion

For definiteness and for simplicity we have analyzed only the following special case which, however, reveals the peculiarities of the considered system (see the schematic diagram in Figure 1):

$$\begin{aligned} \chi_{+A} &= \chi - \Delta\chi & \chi_{+B} &= \chi + \Delta\chi \\ \chi_{-A} &= \chi + \Delta\chi & \chi_{-B} &= \chi - \Delta\chi \end{aligned} \quad (11)$$

It is evident that in this case that the system is symmetric, i.e., if $z = 0$ in the point where $\phi_A = \phi_B$ then

$$\begin{aligned} \phi_A(z) &= \phi_B(-z) & \phi_+(z) &= \phi_-(-z) \\ \varphi(z) - \varphi(0) &= \varphi(0) - \varphi(-z) \end{aligned} \quad (12)$$

Equations 12 are of course valid both for a mixture considered as a continuous one and for a mixture considered as a sequence of elementary layers.

It is convenient to consider the case represented by eq 11, since in this case it is easy to determine the composition of the two phases. Namely, in this case the volume fractions of ions in the two phases are equal to a certain predetermined value $\phi_{\text{ions}}^\infty$:

$$\phi_+(-\infty) = \phi_+(+\infty) = \phi_-(-\infty) = \phi_-(+\infty) = 0.5 \cdot \phi_{\text{ions}}^\infty \quad (13)$$

One only has to make sure that, at the given values χ_{AB} and $\phi_{\text{ions}}^\infty$, each of the two phases is stable, i.e., that it does not segregate. As to the volume fractions ϕ_A^∞ and $\phi_A^{+\infty}$ of the A molecules in the two phases, in this case $\phi_A^{+\infty} + \phi_A^\infty = 1 - \phi_{\text{ions}}^\infty$ (see eq 12), and they are the two roots of the equation

$$\chi_{AB}(1 - \phi_{\text{ions}}^\infty - 2\phi_A) + \ln \frac{\phi_A}{1 - \phi_{\text{ions}}^\infty - \phi_A} = 0 \quad (14)$$

which represents the binodal conditions in the considered symmetric case (11). Equation 14 has the two roots if

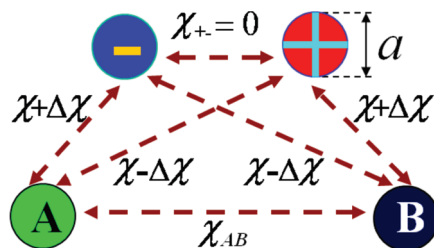


Figure 1. Schematic diagram representing the values of the Flory–Huggins parameters describing the van der Waals interactions of the system’s components.

$$\chi_{AB} > \frac{2}{1 - \phi_{\text{ions}}^\infty} \quad (15)$$

Otherwise, the two phases cannot be formed. (We ignore the root $1 - \phi_{\text{ions}}^\infty = 2\phi_A$ because it has no physical sense).

It should be also noted that in the considered case the equality (14) is nothing else but the equality $\partial f / \partial \phi_A = 0$ (this simplifies the eq 9) and it follows from it besides that

$$\tilde{\phi}(+\infty) - \tilde{\phi}(-\infty) = 2\Delta\chi[\varphi_A(+\infty) - \varphi_A(-\infty)] \quad (16)$$

Figures 2 and 3 represent distributions of components concentrations and potentials near the phase boundary for different values of the parameters $\phi_{\text{ions}}^\infty$ and $\Delta\chi$. We investigated the case $\chi_{AB} = 4$ (the components A and B are rather strongly incompatible) and also supposed for definiteness that $\chi = 0$. One can see that if $\Delta\chi \neq 0$ a double electrostatic layer is formed at the phase boundary: the concentration of cations is higher than the concentration of anions on the side of the boundary where the concentration of A is higher, the concentration of anions is respectively higher than the concentration of cations on the other side. All the plots presented are symmetric since eqs 12 are valid in the considered case.

The concentration profile of cations (or of anions as well) may be divided into two parts. The first part corresponds to the region where concentrations of A and B vary. In this region the cations concentration gradient is the largest. This region is normally only several molecules thick (see Figure 2 IV, V and Figure 3 IV). It can be thicker if the mixture is close to the critical point when the compositions of the two phases do not differ much from each other. In this case the inequality (15) is almost an equality. If the mixture is close to the critical point, the concentrations of the cations and the anions do not differ much from their bulk value and they look like almost symmetrical bells slightly shifted one from another (see Figure 2 VI).

The other part of the cations concentration profile corresponds to the two close to the phase boundary regions in which concentrations of A and B are already constant. In these regions volume fractions of cations (and anions) differ significantly from their bulk value $\phi_{\text{ions}}^\infty$ if the bulk value is small enough. These regions are the broader the smaller is $\phi_{\text{ions}}^\infty$ (compare Figures 2 I, III, IV). In the region where $\phi_A > \phi_B$ the concentration of cations is larger nearer the center of the phase boundary, and in the region where $\phi_A < \phi_B$ it is reversed. (The anions concentration profile is the mirror image of the cations concentration profile.)

The ratio of the cations (anions) maximal concentration to their concentration in the bulk increases with $\Delta\chi$ (compare Figures 3 I and II) and it decreases if the bulk value $\phi_{\text{ions}}^\infty$

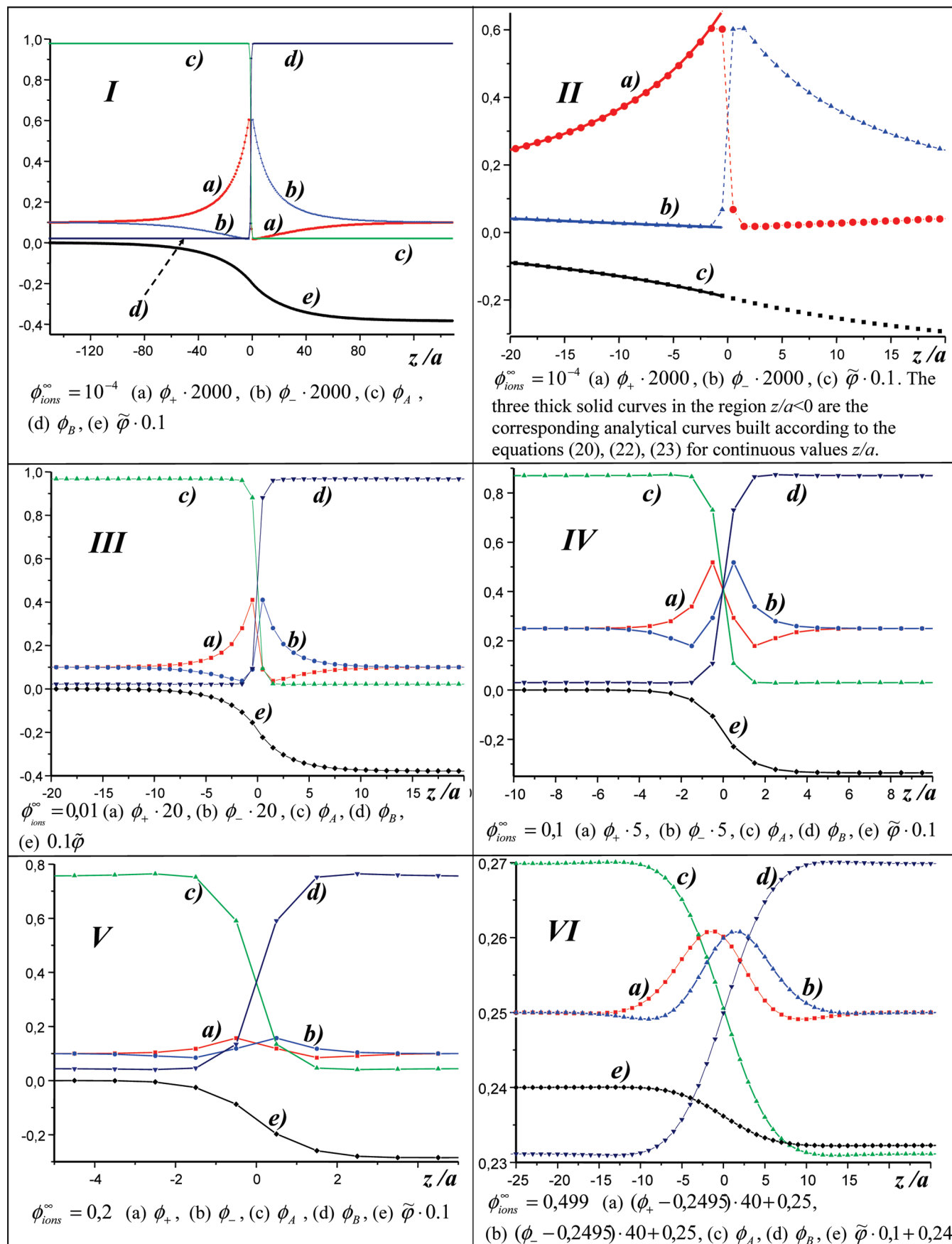


Figure 2. Dependencies of the components volume fractions ϕ_+ , ϕ_- , ϕ_A , and ϕ_B and of the electrostatic potential $\tilde{\varphi}$ on the coordinate z perpendicular to the phase boundary for different values of the parameters ϕ_{ions}^{∞} at $\Delta\chi = 2$, $\chi_{AB} = 4$, and $\chi = 0$.

increases (compare Figures 2 I, III–IV). For example, for the case presented by Figure 3 II the ratio reaches 30. It is interesting

that even if $\Delta\chi = 0$, the concentration of the ions (in this case concentrations of the cations and of the anions are of course

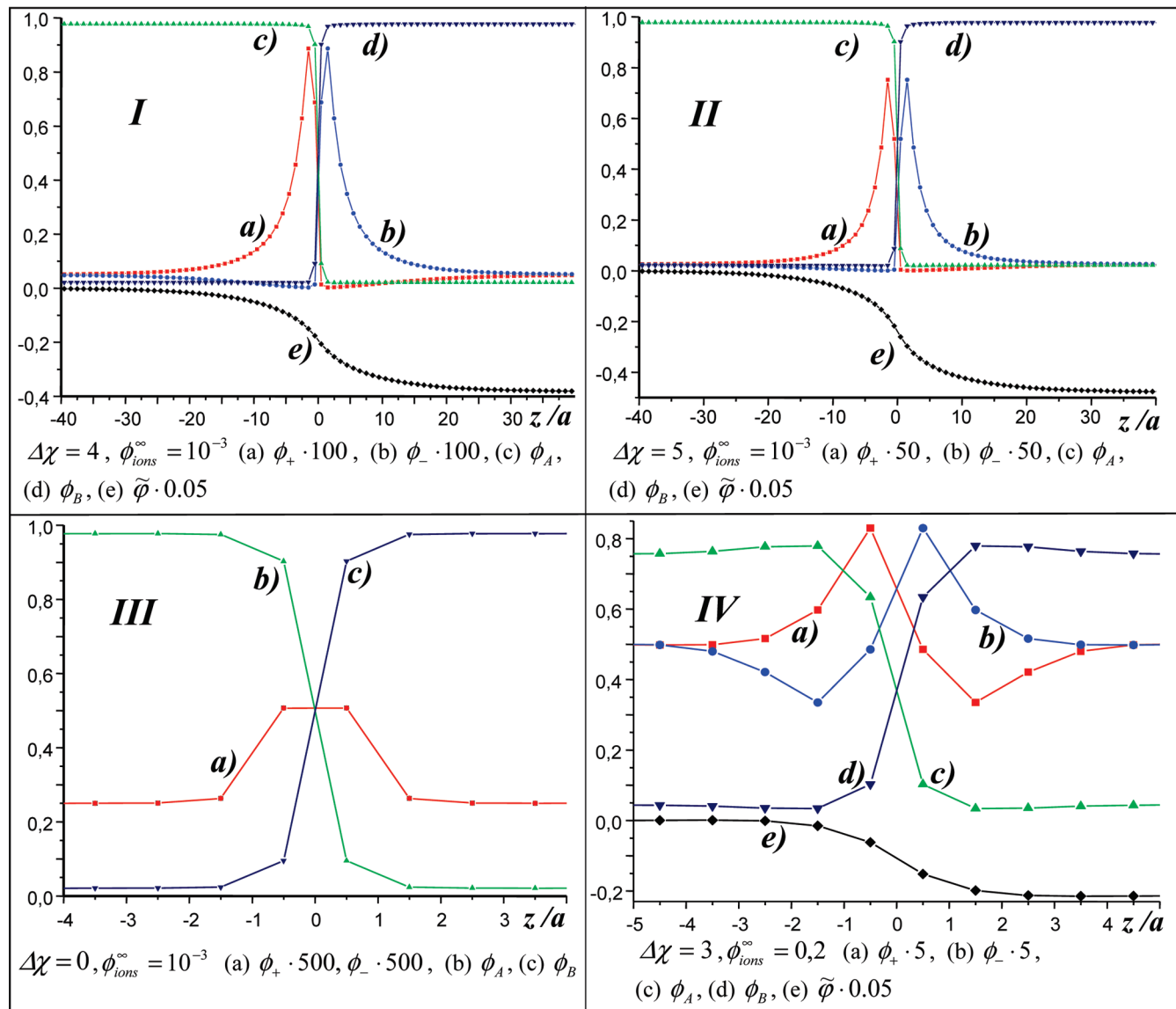


Figure 3. Dependencies of the components volume fractions ϕ_+ , ϕ_- , ϕ_A , and ϕ_B and of the electrostatic potential $\tilde{\phi}$ on the coordinate z perpendicular to the phase boundary for different values of the parameters ϕ_{ions}^∞ and $\Delta\chi$, at $\chi_{AB} = 4$ and $\chi = 0$.

equal to each other in all the points of the mixture) in the center of the phase boundary is a bit larger than their concentration in the bulk (see Figure 3 III). We checked that for all values ϕ_{ions}^∞ , χ , and χ_{AB} .

If $\phi_{ions}^\infty \ll 1$, $\Delta\chi \neq 0$, and χ_{AB} is significantly large (the considered value $\chi_{AB} = 4$ is sufficiently large), the second aforementioned part of the concentration profile can be calculated analytically. In this case the region where concentrations of A and B vary is only several molecules thick and the region where concentrations of cations and anions differ from the bulk value ϕ_{ions}^∞ is many times thicker (see Figures 2 I). Therefore, one can assume that the first of the regions has the zero thickness; it is a plane.

Concentrations of A and B in the bulk on the “left” side of the plane are equal to $\phi_A^{-\infty}$ and $\phi_A^{+\infty}$ (we assume that $\phi_A^{-\infty} > \phi_A^{+\infty}$), and vice versa on the “right” side. One can assume also that in the both half-spaces the concentrations of components are the same in the neighboring elementary layers. One can then simplify eq 1 and after omitting terms that are small because volume fractions of ions are small, one can write the free energies per one elementary cell, $f_{-\infty}$ and $f_{+\infty}$, respectively, for the “left” and “right” half-spaces of the mixture:

$$\frac{f_{\pm\infty}(z)}{kT} = \phi_+(z) \ln \phi_+(z) + \phi_-(z) \ln \phi_-(z) + (\chi \mp \Delta\tilde{\chi})\phi_+(z) + (\chi \pm \Delta\tilde{\chi})\phi_-(z) + \frac{1}{2}\tilde{\phi}(\phi_+(z) - \phi_-(z)) \quad (17)$$

where

$$\Delta\tilde{\chi} = - \frac{\Delta\chi(1 - 2\phi_{ions}^\infty - 2\phi_A^\infty)}{1 - 2\phi_{ions}^\infty} \quad (18)$$

Since chemical potentials of cations and anions in all the points of the mixture are same the following equations are valid for the “left” half-space:

$$\ln \phi_\pm(z) + (\chi \mp \Delta\tilde{\chi}) \pm \tilde{\phi}(z) = \mp\mu_1 - \mu \quad (19)$$

where $\mp\mu_1 - \mu$ are the chemical potentials of cations and anions, respectively, normalized to kT . It follows from the

eqs 13 and 19 and from the assumption $\tilde{\varphi}(-\infty) = 0$ that $\mu_1 = \Delta\tilde{\chi}$ and

$$\phi_{\pm}(z) = \exp(-\chi - \mu \mp \tilde{\varphi}(z)) = 0.5 \cdot \phi_{\text{ions}}^{\infty} \exp(\mp \tilde{\varphi}(z)) \quad (20)$$

If one substitutes the eq 20 in the Poisson equation, one obtains the equation

$$\tilde{\varphi}'' = 2\pi\phi_{\text{ions}}^{\infty}u(e^{\tilde{\varphi}} - e^{-\tilde{\varphi}}) \quad (21)$$

which is nothing but the main equation of the Gouy–Chapman theory (see, for example, refs 31 and 32). In eq 21 we have made a transition to the dimensionless coordinate $\tilde{z} = z/a$.

The solution for of the differential eq 21 for $\tilde{z} < 0$ with the boundary condition $\tilde{\varphi}(-\infty) = 0$ is

$$\tilde{\varphi} = 2 \ln \frac{\exp(2\sqrt{\pi\phi_{\text{ions}}^{\infty}u}[\beta - \tilde{z}]) - 1}{\exp(2\sqrt{\pi\phi_{\text{ions}}^{\infty}u}[\beta - \tilde{z}]) + 1} \quad (22)$$

The constant β can be obtained by means of minimizing the functional of the free energy (17) after substituting into it eqs 20 and 22:

$$\beta = \frac{1}{2\sqrt{\pi\phi_{\text{ions}}^{\infty}u}} \cdot \ln \frac{\exp(0.5 \cdot \Delta\tilde{\chi} - 1) + 1}{\exp(0.5 \cdot \Delta\tilde{\chi} + 1) - 1} \quad (23)$$

It follows from eqs 23, 22, and 20 that the characteristic thickness of the formed double electrostatic layer is $(\phi_{\text{ions}}^{\infty}u)^{-1/2}$ and that

$$\phi_{\pm}(0) = 0.5 \cdot \phi_{\text{ions}}^{\infty} \exp(\Delta\tilde{\chi}) \quad (24)$$

The “left” half-space total charge σ per unit area of the phase boundary is equal to

$$\sigma \frac{ea}{kT} = \sqrt{\pi \frac{\phi_{\text{ions}}^{\infty}}{\pi u}} \cdot \frac{\exp(\Delta\tilde{\chi}) - 1}{2 \exp(0.5 \cdot \Delta\tilde{\chi})} \quad (25)$$

The analytical dependencies represented by eqs 23, 22, and 20 coincide perfectly at $\phi_{\text{ions}}^{\infty} < 10^{-3}$ with the corresponding dependences obtained by means of the numerical minimization of the sequence of elementary layers free energy. For example, the solid curves in Figure 2 II are the analytical ones. One can see that they fit perfectly all the corresponding numerically obtained points except the closest to the center of the phase boundary elementary layers.

As to the phase boundary surface tension, our numerical calculations have shown that it decreases with the increase of $\Delta\chi$ (see Figure 4). The reason is the segregation of the cations and the anions at the phase boundary: the concentration of cations (anions) happens to be higher in the part of the phase boundary transition region where the affinity of the cations (anions) to the surrounding neutral solvent is relatively high and it happens to be lower in the part of the transition region where the affinity of the cations (anions) to the surrounding neutral solvent is relatively low.

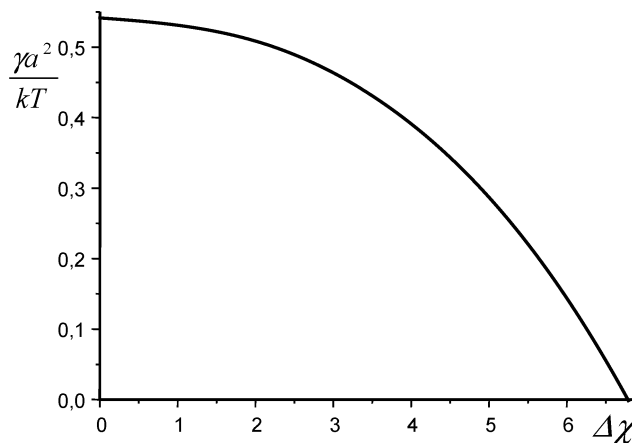


Figure 4. Dependence of the phase boundary surface tension γ on the parameter $\Delta\chi$ at $\phi_{\text{ions}}^{\infty} = 10^{-3}$, $\chi_{\text{AB}} = 4$, and $\chi = 0$.

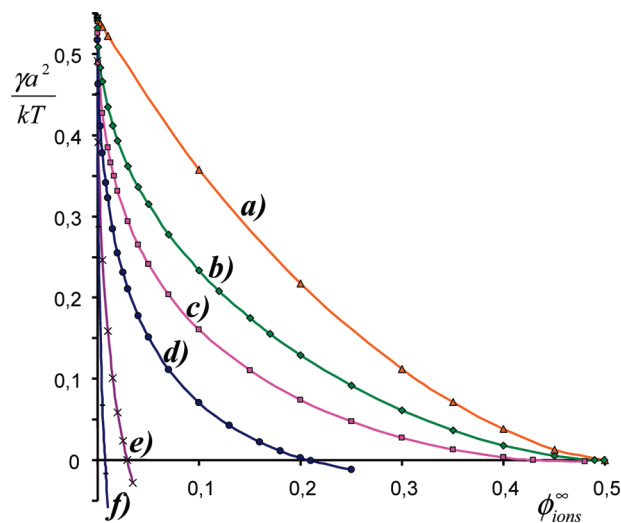


Figure 5. Dependence of the phase boundary surface tension γ on the volume fraction $\phi_{\text{ions}}^{\infty}$ of ions in the bulk at $\chi_{\text{AB}} = 4$, $\chi = 0$, and (a) $\Delta\chi = 0$, (b) $\Delta\chi = 2$, (c) $\Delta\chi = 2.5$, (d) $\Delta\chi = 3$, (e) $\Delta\chi = 4$, and (f) $\Delta\chi = 5$.

In a sense, the IL behaves as a surfactant. But the significant difference between such an IL and a surfactant is that the IL forms at the phase boundary a double electrostatic layer that can be several hundred molecules thick (see Figure 2 I), while a surfactant forms a monomolecular layer at the settled by it interface.

The phase boundary surface tension decreases also with the increase of the IL concentration (see Figure 5). This has a place even if $\Delta\chi = 0$ (see Figure 5, curve a) because the larger $\phi_{\text{ions}}^{\infty}$ is the closer the system is to the critical point ($\phi_{\text{ions}}^{\infty} = 0.5$, see the inequality (15)) where the surface tension turns into zero. If $\phi_{\text{ions}}^{\infty} > 0.5$, the two-phase mixture cannot exist. But the larger $\Delta\chi$ is the faster the surface tension decreases with the increase of $\phi_{\text{ions}}^{\infty}$ (compare the different curves in the figure 5). This is also evidently caused by the aforementioned segregation of ions. Moreover, if $\Delta\chi$ is large enough, the surface tension turns to zero before $\phi_{\text{ions}}^{\infty}$ reaches the critical value 0.5. All the curves in the figure meet in one point at $\phi_{\text{ions}}^{\infty} = 0$, since the surface tension of the phase boundary does not depend on the affinities of the ions to the neutral components A and B, if there are no ions in the system.

The predicted by our theoretical consideration decrease of the phase boundary surface tension caused by addition of ions does not agree with the results of the works^{19,21–23,26} which

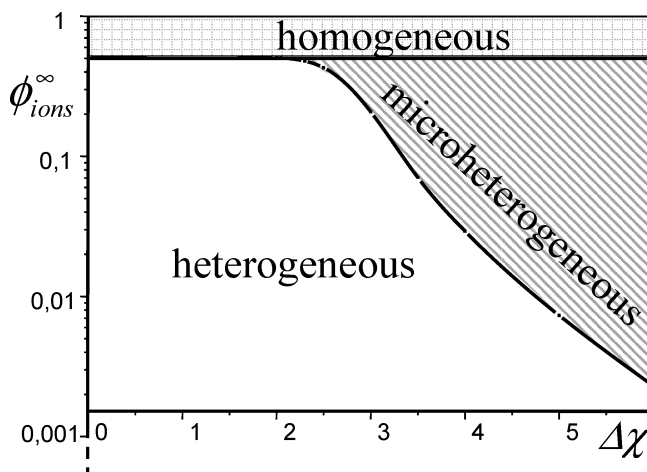


Figure 6. Phase diagram of the mixture's states in the coordinates $(\Delta\chi, \phi_{\text{ions}}^{\infty})$ at $\chi_{\text{AB}} = 4$ and $\chi = 0$.

predict the increase of the surface tension. This is not surprising, since we have not included in our model the image potential. Nevertheless, we believe that our calculations have sense because the influence of the image potential is significant only if the dielectric constants of the components A and B differ strongly from each other. Besides our calculations are valid for high concentrations of ions and reveal the individual effect of the influence on the surface tension of the difference in the cations and the anions affinities to A and B. It should be noted in addition that the evidently important factor of the affinities difference has not been at all taken into account in the works.^{19,21–23}

The curves in Figure 5 that correspond to $\Delta\chi = 2.5$, $\Delta\chi = 3$, $\Delta\chi = 4$, and $\Delta\chi = 5$ are drawn to negative values of the surface tension γ . This means that in some cases the components' concentration profiles at the phase boundary that correspond to the minimum of the free energy can be determined by means of our numerical method even if the surface tension calculated thereafter happens to be negative.

Of course, in reality the surface tension cannot be negative. Otherwise, an unlimited growth of the phase boundary surface tension would be favorable and the two phases would not stop splitting and intermixing. A negative value of γ obtained in the calculation means that at the corresponding values of the parameters the two phases cannot coexist.

On the other hand, if the inequality (15) is fulfilled, the mixture cannot be homogeneous as well. Thus the mixture must be microheterogeneous. In fact, the induced by the addition of a surfactant transformation of a biphasic system into a microheterogeneous system is a well-known phenomenon (see, for example, ref 33). In this sense, the "surface active" IL considered by us is not an exception.

The corresponding phase diagram of the mixture's states in the coordinates $(\Delta\chi, \phi_{\text{ions}}^{\infty})$ for the parameters values $\chi_{\text{AB}} = 4$, $\chi = 0$ is presented in the Figure 6. One can see that at a given value $\Delta\chi$ if $\phi_{\text{ions}}^{\infty}$ is very small the mixture is heterogeneous, if $\phi_{\text{ions}}^{\infty}$ exceeds a certain threshold value, the mixture becomes microheterogeneous, and if $\phi_{\text{ions}}^{\infty}$ grows further and exceeds the critical value 0.5 (see inequality (15)), the mixture becomes homogeneous. Unfortunately, the accuracy of our method and the computing power of a PC do not allow us to find out if a microheterogeneous state is possible at $\Delta\chi < 2$. Probably, at the small values of $\Delta\chi$ the homogeneous and the heterogeneous states have a common border on the phase diagram. At least our calculations have shown that at $\Delta\chi = 2$ the mixture is heterogeneous even at $\phi_{\text{ions}}^{\infty} = 0.499$.

Conclusions

We have considered theoretically a two-phase system consisting of nonionic components A and B that are incompatible with each other and of an IL. We have shown that if the IL's cations have a higher affinity for A than for B and the IL's anions vice versa have a higher affinity for B than for A, then a double electrostatic layer is formed at the phase boundary. The width of the double layer increases as the concentrations of ions approach either zero or the value corresponding to the critical point. The ratio of the maximal cations (anions) concentration in the layer to their concentration in the bulk far from the boundary increases with decreasing concentration of IL and with increasing difference in the affinities of the cations and the anions to A and to B.

We have also shown that the surface tension of the phase boundary decreases with increasing difference of the affinities and with increasing concentration of the IL. The surface tension can even reach zero at a concentration of IL lower than the one corresponding to the critical point, which means that, at the corresponding values of the parameters characterizing the system, the mixture is microheterogeneous. One can say that such an IL behaves as a surfactant, but instead of a monomolecular layer, it forms at the phase boundary a double electrostatic layer, which can be up to several hundred molecules thick.

In this work we have considered only the special symmetric case when the affinities of cations for A and of anions for B, and vice versa, are the same. In a forthcoming work we are going to consider the general case.

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