PHASE EQUILIBRIA IN BINARY SYSTEMS COMPRISING IONIC LIQUIDS: THEORETICAL STUDY

Dissertation

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Die Dissertation „Phasengleichgewichte in Binärsystemen mit ionischen Flüssigkeiten: theoretische Betrachtung" von Artem A. Aerov besteht aus einer Einleitung, einer Literaturrecherche, vier neu erarbeiteten Abschnitten, den Schlussfolgerungen, einem Anhang bestehend aus zwei Kapiteln, einem Literaturverzeichnis und den Danksagungen.

In der **Einleitung** wird die technische Bedeutung ionischer Flüssigkeiten und die Relevanz theoretischer Untersuchungen diskutiert. Die Bedeutung der vorliegenden Arbeit und deren Ziele werden erläutert.

Die **Literaturrecherche** (Kapitel 1) setzt sich aus zwei Teilen zusammen. Der erste Teil stellt eine kurze Übersicht über die aus Experimenten bekannten interessantesten und wichtigsten Eigenschaften der ionischen Flüssigkeiten und deren Anwendungen vor. Detailliert werden diejenigen Arbeiten betrachtet, die sich mit den Wechselwirkungen ionischer Flüssigkeiten mit Kohlenstoffnanoröhrchen beschäftigen. Der zweite Teil widmet sich den theoretischen Arbeiten und Computersimulationen, in denen Systeme betrachtet werden, die Ionen enthalten. Eine besondere Aufmerksamkeit wird auf diejenigen Arbeiten gelegt, in denen Phasengleichgewichte und Grenzflächenphänomene mit jeweils einer Komponente in Form einer ionischen Substanz untersucht werden. In der Mehrzahl dieser Fälle wird das so genannte „restricted primitive model" verwendet. Darüber hinaus werden Studien betrachtet, in denen der Einfluss ionischer Beimischungen auf die Oberflächenspannung von Zweiphasensystemen untersucht wird.

In den folgenden vier Kapiteln werden die neuen Ergebnisse aus dieser Arbeit vorgestellt. Die Lösung der in dieser Arbeit betrachteten Probleme basiert auf dem Flory-Huggins Gitteransatz.

Im **Kapitel 2** wird ein Erklärungsansatz vorgestellt, der zeigt, wieso ionische Flüssigkeiten gute Lösungsmittel für verschiedene Stoffklassen sind. Eine homogene Mischung einer ionischen Flüssigkeit und einer zufälligen nicht-ionischen Flüssigkeit wird betrachtet. Die Spinodale der makroskopischen Trennung wird erstellt und es wird gezeigt, dass mit zunehmender Bindungsenergie der Kationen und Anionen der ionischen Flüssigkeit, die durch die van-der-Waals-Kräfte hervorgerufen wird, also mit steigender Inkompatibilität, die Löslichkeit der nicht-ionischen Flüssigkeit in der ionischen Flüssigkeit zunimmt.

Das **Kapitel 3** behandelt die Studie einer Mischung von ionischen und nicht-ionischen Flüssigkeiten, die aus zwei makroskopisch getrennten Phasen besteht. Die Konzentrationen der Komponenten in den Bulkphasen sowie die Konzentrationen der ionischen Spezies an der Phasengrenze werden bestimmt. Zusätzlich wird die Oberflächenspannung der Grenzfläche berechnet.

Es wird gezeigt, dass sich an der Grenzfläche eine doppelte elektrostatische Schicht bildet, und dass die elektrostatische Energie umso größer ist, desto größer die Differenz der Affinität der Kationen und Anionen der ionischen Flüssigkeit zu den neutralen Molekülen ist. Außerdem wird gezeigt, dass die Oberflächenspannung an der Phasengrenzfläche mit zunehmender Differenz der Affinitäten abnimmt und sogar auf Null absinken kann. Folglich wird bewiesen, dass es möglich ist, dass ab einem bestimmten Grenzwert dieser Differenz die Bildung mikroheterogener Strukturen in der Mischung möglich ist, da in diesem Fall ein zweiphasiges System nicht mehr stabil ist.

Das **Kapitel 4** ist einer zusätzlichen Studie über die im Kapitel 3 festgestellte Möglichkeit der Bildung mikroheterogener Strukturen in einer Mischung einer ionischen Flüssigkeit mit einer nicht-ionischen Flüssigkeit gewidmet. Die Stabilität des räumlich homogenen Zustands gegenüber der mikroskopischen Trennung wird zusätzlich durch die Methode der Random-Phase-Approximation analysiert. Das

Ergebnis aus Kapitel 3 wird dadurch bestätigt. Konkret wird bewiesen, dass die Bildung der mikroheterogenen Mischung ionischer und nicht-ionischer Flüssigkeiten möglich wird, wenn die Differenz der Affinitäten der Kationen und Anionen der ionischen Flüssigkeit zu den neutralen Molekülen einen bestimmten Grenzwert überschreitet.

Das **Kapitel 5** erweitert die grundsätzliche Idee der Kapitel 3 und 4 für den Fall, wenn ein Gel-Netzwerk als zweite Komponente an die Stelle der nicht-ionischen Flüssigkeit tritt. Dazu wird die Quellung eines Mikrogels mit immobilisierten Kohlenstoffnanoröhrchen in einer ionischen Flüssigkeit betrachtet. Die Nanoröhrchen verhalten sich im verwendeten Modell als ein Netzwerk von Leitern, das verhindert, dass die nicht kompensierten Ionen innerhalb des Gels sich gegenseitig abstoßen. Es wird gezeigt, dass die Quellrate des Mikrogels von dessen Größe abhängt, falls ein Unterschied in den Affinitäten der Kationen und Anionen der ionischen Flüssigkeit zum Gel-Netzwerk besteht. Wenn die Affinität der ionischen Flüssigkeit als Gesamtes zum Gel-Netzwerk geringfügig höher ist als die Affinität, bei der sich das Gel in einem normalen Ein-Komponenten-Lösungsmittel zusammenfalten würde, dann existieren kleinere Mikrogele im zusammengefalteten Zustand und größere Mikorgele im aufgequollenen Zustand in der betreffenden ionischen Flüssigkeit.

In den Schlussfolgerungen werden die wichtigsten Ergebnisse dieser Arbeit wieder zusammengefasst. Details der komplexen mathematischen Herleitungen sind in den beiden Kapiteln des Anhangs dargestellt.

The abstract of the PhD thesis "Phase Equilibria in Binary systems comprising Ionic Liquids: theoretical study."

The PhD thesis "Phase Equilibria in Binary systems comprising Ionic Liquids: theoretical study." written by Artem A. Aerov contains introduction, literature review, four original parts, conclusions, two appendices, list of references, and acknowledgements.

In the **introduction** the significance of ionic liquids (ILs) in technology and importance of their theoretical investigation is discussed. Relevance of the present thesis and its objectives are explained.

The **literature review** (Chapter 1) consists of two parts. The first part is a brief review of the known from experiment most interesting and important properties of ILs and their applications. In more detail the works are discussed in which phenomena are considered that are connected with interaction of ILs and carbon nanotubes. The second part is devoted to theoretical and computer simulation works in which ion containing systems have been studied. Particular attention is paid to the works in which phase equilibrium and phase boundaries in binary systems comprising an ionic substance as one of the components are considered. In the majority of these works the so-called restricted primitive model is used. Besides those works are considered in which influence of an ionic admixture on the surface tension in a biphasic system is investigated.

In the next four chapters the original results are presented. Solution of all the problems considered therein is based on the Flory-Huggins type lattice approach.

In the **Chapter 2** an explanation is proposed of why many ILs are good solvents for different types of solutes. A homogeneous mixture of an IL and an arbitrary nonionic liquid (nIL) is considered. The spinodal of the mixture's macrophase separation is built and it is demonstrated that the higher is the energy of

the IL's cation and anion contact caused by their Van der Waals interaction, i.e. the stronger is their incompatibility, the stronger is the solvent power of this IL with respect to the nIL.

In the **Chapter 3** the study of a macroscopically phase separated mixture of an IL and a nIL is presented. The components concentrations in the two phases and the ions concentrations profiles near the phase boundary are determined. Besides, the surface tension of the boundary is calculated.

It is demonstrated that a double electrostatic layer is formed at the boundary and its electrostatic energy is the higher the higher is the difference in the affinities of the IL's cations and the IL's anions to the neutral molecules. It is also demonstrated that the surface tension of the phase boundary decreases with the growth of the difference and it can even reach zero. Hence it is proved that if the difference exceeds a certain threshold value then formation of a microheterogeneous structure is possible in the mixture, since a biphasic system can't exist any more in this case.

The **Chapter 4** is devoted to an extra study of the found in the chapter 3 possibility of a microheterogenous structure formation in the mixture of an IL and a nIL. The stability of the mixture's spatially homogeneous state towards microphase separation is analyzed additionally by means of the random phase approximation method. The result of the chapter 3 is corroborated. Namely it is proved that the formation of the microheterogeneous IL/nIL mixture becomes possible if the difference in the affinities of the IL's cations and the IL's anions to the neutral molecules exceeds a certain threshold value.

The **Chapter 5** extends the main idea of the chapters 3 and 4 for the case when a gel network acts as the second component in the system instead of a nIL. The swelling in an IL of a microgel with immobilized carbon nanotubes is studied. The nanotubes act in the applied model as a network of conductor that doesn't allow

uncompensated ions inside the gel to repel each other. It is demonstrated that the swelling ratio of the microgel depends on its size if there is a difference in affinities of the IL's anions and the IL's cations to the network of the gel. If the affinity of the IL as a whole to the network is a bit higher than the affinity at which the gel would collapse in a normal one-component solvent then a smaller microgel is in the collapsed state in this IL and a larger microgel is in the swollen state in this IL.

The main results of the thesis are summarized in the Conclusions. Details of the most cumbersome mathematical expressions derivations can be found in the two appendices.

Contents.

Introduction.

The present dissertation is devoted to theoretical study of effects connected with ions equilibrium distribution in systems comprising an ionic liquid (IL) as one of the components.

Relevance of investigation of ILs is in the first place caused by the possibility of utilization of ILs in environment friendly technologies. ILs are treated along with supercritical carbon dioxide as most prospective reaction media allowing significant decrease of the environment pollution and improvement of such reaction characteristics as speed, yield and selectivity (in comparison with traditional organic solvents).

Majority of liquids we normally have to do with regardless of their being polar or nonpolar consist of molecules. But ionic liquids consist of ions only and nevertheless they are liquid at normal conditions (room temperature and atmospheric pressure). For this reason one could reasonably suppose that ionic liquids possess a number of unique properties that are not inherent to common molecular liquids. This happens to be so indeed. Namely, for example, ILs have a very low vapor pressure. This eliminates the problem of technological equipment hermetization and makes the technological processes more ecologically safe. For the same reason ILs can be used as lubricants and as plasticizers.

This peculiarity of ILs is supplemented by their other important property lying in the fact that many of ILs solubilize easily different polar as well as nonpolar substances. The latter property in itself makes ILs more promising solvents as the traditional ones.

Besides, there is a possibility to produce ILs with desirable properties by means of combining different pairs of cation and anion that were synthesized separately.

ILs are successfully utilized in biphasic catalysis when reaction takes place at the phase boundary of an IL, containing the catalyst, and a nonionic liquid containing the substrate. One of the most outstanding developments of chemical technology in the field of ionic liquids is the invention of the new cellulose processing technique in which an IL is used as the solvent of cellulose. It should also be noticed that at present it is intensively investigated whether ILs can be useful for the solution of the important scientific and technical problem of fuel cells creation. Furthermore it has been already proven that ILs are very promising as electrolytes for supercapacitors.

Very interesting are phenomena connected with interaction of ILs and carbon nanotubes. It has been found out that a dispersion of the nanotubes in an IL forms a physical gel. Besides, an actuator can be formed by two thin layers of such a gel which are separated by the third thin layer of a polymer gel impregnated with the same IL. If voltage is applied to the two surface layers the three-layered film bends.

Although first ILs were known already in 19-th century, they became a popular object of scientific research as recently as in the very end of the 20-th century. Number of publications on the subject of ILs is already large and it grows rapidly. But the majority of these papers have to do with synthesis and experimental investigation of ILs properties. There are also a few works on computer simulation of several individual ILs. And the theoretical study of ILs is nowadays on an early developmental stage. For example, a universally acknowledged theoretical model describing some general properties of ILs as a whole class of substances still doesn't exist. Majority of theoretical works devoted to study of electrolyte systems have to do with low concentrations of ions, while it is evident that if one needs to work out a theory describing properties peculiar to ILs it is crucial to allow for the fact that volume fraction of ions in the mixture can approach unity.

In the present dissertation the theory has been developed that describes generally several properties of ILs as a whole class of substances. The theory is

based on a Flory-Huggins type lattice model. In the second chapter of the text, an explanation is proposed of why many ILs are good solvents for different types of solutes. The explanation is based on the ionic nature of an IL and on the peculiarities of the ionic liquid's cations and anions interaction. The proposed approach allows to predict qualitatively solvent power of an IL in respect to an arbitrary solute. Utilization of the approach can significantly facilitate the experimental search of the most strong solvents among ILs. This seems to be rather important while it is possible to synthesize an enormous number of different ILs, and experimental investigation of the properties of all of them would take a long time.

The third chapter of the dissertation text contains an elaboration of the model proposed in the second chapter. Therein properties of the phase boundary between an IL and a nonionic liquid (nIL) are considered. It is investigated how the properties depend on the difference in the interactions of the IL's cations and the IL's anions with the molecules of the nIL. This part of the present dissertation work also seems to be relevant because it is known that IL based liquid-liquid biphasic catalysis is promising and in some cases has been already proved to be very effective. Inter alia in the third chapter the surface tension coefficient of the phase boundary is calculated, and it is shown that the coefficient can be negative at some values of parameters describing the system. Negative value of the surface tension coefficient means that the mixture of the IL and the nIL can't consist of two separate macrophases, and a microheterogeneous structure must be formed in it.

Microheterogeneous mixtures including an IL as one of the components have been already observed in experiment but haven't yet found a practical application. Nevertheless it is evident that they can be very useful. Namely, if one somehow creates a microheterogeneous analogue of an IL based liquid-liquid biphasic catalytic system, the whole volume of such a reaction mixture will act as a set of nanoreactors having a very large total surface area what provides an easy access of

reagents into the reaction zone. Reaction rate in such a microheterogeneous system is to be many times higher than in an analogous biphasic system.

Therefore, the fourth chapter of the dissertation is devoted to an extra study of the found in the third chapter possibility of a microheterogenous structure formation in the mixture of an IL and a nIL. Therein possibility of a microphase separation in the homogeneous mixture of the two substances is additionally investigated by means of the random phase approximation method (RPA). The results obtained in the third and in the fourth chapters are in agreement.

The last (the fifth) chapter of the dissertation is the extension of the third chapter for the case when a gel network acts as the second component in the system instead of a nIL, i.e. the IL acts as the solvent in which the gel is immersed. The considered gel comprises polymer network and carbon nanotubes that form a conducting network. It is investigated how the swelling ratio of the gel depends on the difference in the interactions of the IL's cations and the IL's anions with the gel network. It is demonstrated that in some cases the size of the gel particle can be the factor determining if the gel will be in the collapsed or in the swollen state. The predicted in the fifth chapter phenomenon complements the range of interesting phenomena connected with interaction of ILs and carbon nanotubes.

Main objectives of the present dissertation work are the following:

1. Investigation of the influence of the interaction nature of cations and anions of an IL on the IL's solvent power within the framework of the Flory-Huggins lattice approach

2. Study of the phase boundary between an IL and a nIL. Namely, determination of the components concentration profiles at the boundary and determination of the surface tension of the boundary. Investigation of the phase boundary properties dependence on the interaction nature of the IL's ions and the molecules of the nIL.

3. Search of the values of parameters describing the interactions of the IL's cations, the IL's anions and the nIL's molecules at which in the mixture of the IL and the nIL a microheterogeneous system is formed.

4. Investigation of the behavior of a polymer gel with immobilized carbon nanotubes in an IL. Namely, investigation of the gel swelling ratio dependence on the interaction nature of the IL's ions and the gel network.

The dissertation text consists of introduction, five chapters, references, and two appendixes in which details of the most cumbersome mathematical expressions derivations are presented. The text contains 115 pages including figures, table of contents and references.

The text is organized as follows. The first chapter is the literature review consisting of two parts. The first of the parts is the review of some experimental works and reviews where most important and interesting properties of ILs and their possible applications are reported. In more detail those works are discussed in which phenomena are considered that are connected with interaction of ILs and carbon nanotubes. In the second part the theoretical and computer simulation works are considered in which ion containing systems have been studied. Particular attention is paid to the works in which phase equilibriums and phase boundaries are considered in binary systems comprising an ionic substance as one of the components. In the majority of the reviewed works the so-called restricted primitive model is used. Besides those works are considered in which an ionic admixture influence on the surface tension in a biphasic system is investigated. The already mentioned chapters 2-5 contain original results obtained by the author.

The main results of the present dissertation work have been published in three papers. One more paper has been submitted. Additionally the results have been reported on six international conferences.

1. Literature Review.

1.1 Properties of ionic liquids.

ILs are substances that are liquid at normal conditions (room temperature and atmospheric pressure) and consist of ions only [1,2]. Previously two different terms "ionic liquids" and "molten salts" were used to identify the same substances. Later a definition has been formulated [3] to differentiate two different classes of liquids composed entirely of ions. According to the definition ILs are the substances with the melting point less than 100 ^{o}C and molten salts have a higher melting temperature. Molten salts are highly viscous and are very corrosive. As it is much more convenient to use in chemical technology solvents that are liquid at normal conditions ILs and not molten salts are more popular in scientific study.

Normally ILs consist of a large organic cation and a small inorganic anion [3]. The cation usually has a functionalized side chain [4]. The charge of the cation is surrounded by a bulky shell of neutral atoms. Therefore distance between the opposite charges of neighboring cations and anions in an IL is rather large, and at room temperature the energy of the ions electrostatic attraction happens to be not high enough in comparison with the thermal motion energy. This is the first reason why ILs don't crystallize at room temperature. The other reason is that an IL's cations significantly differ in size from the anions and are strongly asymmetric [4]. Melting temperature of an IL depends strongly on the degree of the IL's cations skewness, namely on the nature of its side chain. Although ILs do not crystallize at room temperature, some of them that comprise the 1,3 dialkylimmidazolium cation (an example is presented in the upper right corner of the Figure 1) are believed to form a hydrogen-bonded superstructure in the liquid state [5].

ILs can be divided into two classes: protic ionic liquids (PILs) and aprotic ionic liquids (AILs). PILs are a subset of ILs that are produced through a combination of a Brønsted acid and a Brønsted base. The key property that

distinguishes PILs from AILs is the proton transfer from the acid to the base, leading to the presence of proton-donor and -acceptor sites [6]. In PILs the proton transfer from the Brønsted acid to the Brønsted base is reversible. That's why in PILs in the equilibrium state there is always a part of electroneutral acid and base species present. It is generally assumed that a PIL can be termed as an IL if it has not more than 1% of neutral species. If concentration of neutral species in a PIL is higher it is better to treat it as a mixture of an IL and a nonionic liquid [7].

One of the most important peculiarities of ILs is their very low volatility [8]. AILs are composed entirely of ions, and for this reason possess extremely low volatility. Until now only a few of them have been distilled at a high temperature and low pressure [9]. PILs are distilled easier than AILs because they contain a fraction of neutral molecules that are easier transferred to the gas phase [6]. Main advantage of the low volatility of ILs is the possibility of their application in industrial chemical processes as "green" solvents that do not penetrate into the environment [10]. However, there are also other applications of ILs that are straightforwardly connected with their low volatility. Namely, ILs can be used as lubricants, plasticizers, and heat transfer fluids [11].

The other indispensable property of ILs is that many of them are good solvents for many substances both polar and nonpolar [1,3]. The high solvent power of ILs is the property that allowed the development of the new effective cellulose processing technique [12]. In this technique cellulose fibers are dissolved in an IL without any chemical pretreatment [12]. The high solvent power of ILs in respect to both polar and nonpolar solutes also makes them promising in application to gas chromatography. It has been demonstrated [13,14] that stationary phases formed by some ILs have a dual property acting as a polar stationary phase with polar compounds and as a low-polarity phase with nonpolar compounds. Moreover some chiral ILs have also been used as stationary phases for separation of chiral

compounds [15]. In the third chapter of the present dissertation a possible explanation of ILs high solvent power is proposed [16].

The low volatility of ILs and their high solvent power are complemented by another helpful for chemical technology property of ILs. Namely, majority of ILs are nonflammable [17].

There are almost unlimited possibilities of creating ILs with different properties by means of combining different pairs of cation and anion. Since functional side chains of cations can be varied already now more than a million of different ILs can be synthesized [18]. Also the so-called mixtures of two ILs with a common ion may possess useful properties. These liquids are composed of ions of three different types and more than 10^{12} substances of this type can be hypothetically produced [18]. It is impossible in practice to produce all these substances and study their properties in experiment. That's why it is important to have a criterion for preselection of ILs that are likely to possess interesting useful properties prior to investigating the ILs experimentally. This is one of the reasons of why the theoretical models proposed in the present dissertation [16,19,20] may be useful.

ILs are electrolytes but at room temperature ion conductivity of ILs is not very high due to their high viscosity [21]. Nevertheless ILs are promising in application to electrochemical processes [17] as they can act simultaneously as a solvent and as an electrolyte. Besides ILs can be used as electrolytes in supercapacitors [22] and in solar cells [23].

PILs are able to conduct protons and in distinction from water their boiling temperature is higher than 100 ^{o}C. For this reason utilization of PILs in proton conducting membranes of fuel cells is more convenient than utilization of water solutions of electrolytes. That's why application of PILs to production of fuel cells is intensively studied [6].

In chemical technology ILs probably have proved to be most useful in application to the organometallic biphasic catalysis. The most popular ILs used in

the biphasic catalysis (and, probably, in the majority of the other applications) are the tetrafluorborate and hexafluorphosphate of 1-butyl-3-methylimidazolium (noted in literature as (BMI)BF$_4$ and (BMI)PF$_6$ respectively). (The structure of the BMI cation is presented in the upper right corner of the Figure 1.) In the process an IL is the phase in which a transition metal based catalyst is immobilized. The substrate is dissolved in the coexisting phase – in a nonionic organic solvent. The fact is that transition metal complexes, which act as catalysts, are well soluble in the ILs [3] and they are not extracted from the ILs by nonpolar organic solvents. Besides it is believed that transition-metal complexes do not undergo in the ILs solvation and solvolysis, while these phenomena are usually present in molecular solvents such as water and acetonitrile [3]. It was determined that in most of the cases the reaction occurs preferentially in the IL phase as the substrate diffuses inside the IL from the organic solvent. Theoretical description of such a biphasic system consisting of an IL and a nIL is proposed in the third chapter of the present dissertation [19].

Another substantial advantage of the IL based biphasic catalytic systems lies in the ease of the processes of product separation and catalyst recovery. As the catalyst is not extracted from the IL phase, this catalyst containing phase can be easily separated by filtration from the organic phase containing product. Moreover in some cases when the reaction mixture is cooled the IL with immobilized catalyst freezes earlier than the other phase and, hence, it can be separated from the latter one simply by decantation [3].

The number of the catalytic mixture reuses can be additionally increased by means of covalent linking the catalytic complexes and ions of the IL. Thus the washing out of the catalytic centers into the organic phase is even more suppressed [24].

One more important for chemical industry property of ILs is their ability to catalyze some reactions thus acting simultaneously as a solvent and as a catalyst [6].

In ILs the ordering of molecules in the layer adjacent to a gas phase has been observed [25]. In the work [25] a neutron reflection study has been performed to examine the structure of the free surface of two ILs: 1-butyl-3-methylimidazolium tetrafluoroborate and 1-octyl-methylimidazolium hexafluorophosphate. It has been determined that in the 50 Å thick surface layer an ordering of the ions takes place, namely, several layers enriched with headgroups or alkyl chains are formed.

Mixtures of IL and nIL usually possess an upper critical solution temperature [26,27]. However, in some cases the two-phase regions on the temperature-concentration phase diagrams have been found to be closed [28]. The other interesting fact is that ternary mixtures IL-ethanol-water can be homogeneous while binary mixtures of the same IL with water or ethanol segregate [29].

Probably the most interesting properties of ionic liquids from the point of view of a physicist are associated with interaction of ILs with carbon nanotubes. Carbon nanotubes are cylindrical molecules composed of carbon atoms. Their diameter can be as little as 1 nanometer and their length can reach many micrometers [30]. They consist of carbon atoms and can essentially be thought of as a singe layer of graphite that has been wrapped into a cylinder. The main properties of carbon nanotubes are their record-high elastic modulus and conductivity. The latter one seems to be most important in connection with the interaction of the tubes with ILs. Depending on the chirality of the hexagonal carbon lattice along the carbon nanotube it can be a metal or a semi-conductor. It turns out that that about two-thirds of the tubes are semiconducting and one-third are metallic [30]. Carbon nanotubes can be single-wall (SWNTs) or multiwall. The SWNTs are a more interesting object of scientific study because of their greater aspect ratio [31].

First interesting phenomenon associated both with ILs and SWNTs is the formation of a physical gel by SWNTs ground in imidazolium ion-based ILs (the so-called bucky gels). In the work [32] gels composed of an IL and SWNTs were produced. They contained only 0.5% wt of SWNTs. Usually SWNTs exist as

bundles. But upon gelation in the ILs the bundles exfoliate to form much finer bundles [32]. The thus obtained gels are thermally stable and they don't shrivel, even under reduced pressure. The exfoliation is very probably caused by the ILs high solvent power and the stability of the gels is obviously caused by the low volatility of ILs. Such physical gels could be obtained neither by means of grinding SWNTs in common organic solvents nor by means of grinding other carbon allotropes such as graphite (1 to 2 μm) and C_{60} in ILs [32] .

It is interesting that the rheological study of the gels [32] has proved that their elasticity is governed more likely not by the entanglement of the SWNTs bundles but by a large number of physical cross-links between the bundles, for which molecular ordering of ILs is likely to be responsible. The unimodal crystal growth in the gel at low temperature observed besides in the work [32] results most likely from controlled nucleation initiated by this local molecular orientation. According to the work [32] authors point of view the molecular ordering is caused by the ability of SWNTs to *orient the imidazolium ions on their π-electronic surfaces by way of a possible "cation- π" interaction*.

For our opinion, there may be another explanation of appearing of the physical cross-links between the nanotubes that doesn't involve any structural features of ILs or SWNTs. Namely, a conductor attracts a charged particle by the charge induced on the conductor by the very particle. So, a charged particle (IL's ion), or a pair of two oppositely charged particles can act as a sticker between two conducting parts (SWNTs).

An extension of the finding is the synthesis of the physical gel from SWNTs and a polymerizable IL with the further polymerization of the IL [31]. Interesting feature of the thus obtained gel lies in the fact that its Young's modulus is many times higher than the one of a reference gel polymerized without SWNTs. A 7% content of SWNTs could cause a 120-fold enhancement of the Young's modulus.

The reason of this effect lies also in the interaction of the IL polymer network and the SWNTs.

An important in the framework of the present dissertation fact mentioned in the works [31] and [32] is that the described gels containing SWNTs are highly electroconductive in contrast to the reference gels containing no SWNTs, that are insulators. Furthermore, in the work [31] it has been determined by means of scanning electron microscopy and atomic force microscopy that SWNTs are uniformly dispersed without agglomeration in the matrix of the investigated gel and they form a crosslinked network. This means that the considered in the fifth chapter of the present dissertation gel with immobilized SWNTs forming a conducting network can really exist.

As to polymers composed of monomer units that are ions of an IL, let us mention another interesting fact connected with them. It has been found out in the work [33] that some of these polymers in solid state at room temperature are good selective absorbers of carbon dioxide with higher absorption capacity than ILs [34]. Sorption and desorption are very fast and the desorption by vacuuming is completely reversible. It has been proved that the sorption takes place mostly in the bulk of the polymer particles and not at their surface. The polymers are promising as solid absorbent for carbon dioxide separation.

The other very interesting object that can be created with using SWNTs and ILs is an actuator [35]. An actuator is a thin film consisting of three layers. The central layer is a polymer gel impregnated with an IL. The two surface layers comprise the same components and a dispersion of SWNTs in addition. The surface layers act as electrodes. If a voltage is applied to them the actuator bends in the direction of the cathode (see Figure 1). The edge of a 0.28 mm thick and 15 mm long film can shift 10 mm away from its initial position when the 3.5 V voltage is applied [35].
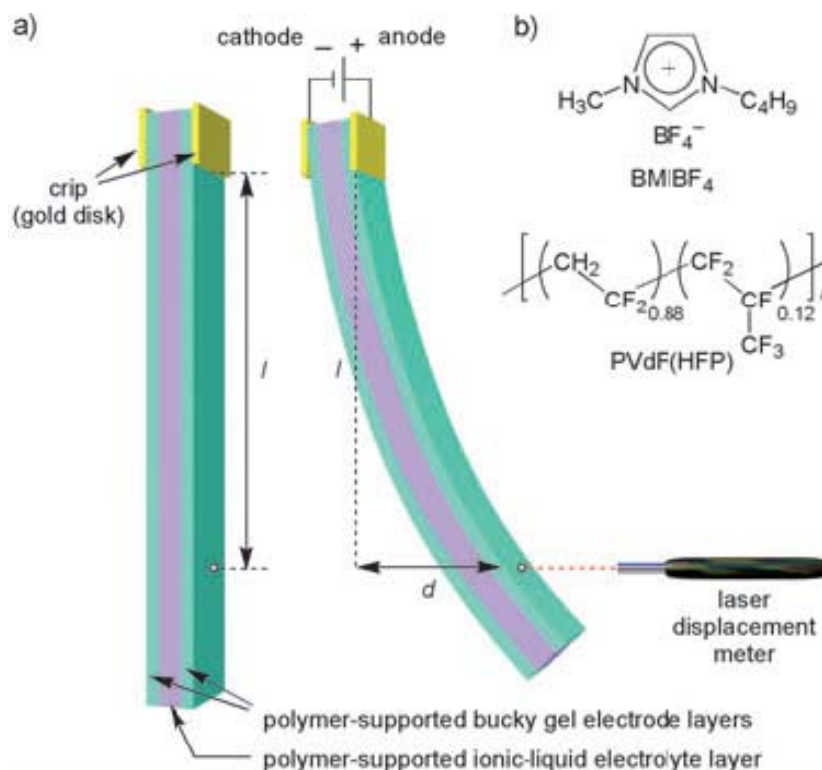
Figure 1. Bucky-gel-based bimorph actuator. *a*) Schematic structure of the actuator strip composed of a polymer gel supported ionic-liquid electrolyte layer sandwiched by bucky-gel electrode layers. *b*) Molecular structures of the IL BMIBF$_4$ and of the gel polymer PVdF(HFP). [35]

A possible explanation of the phenomenon is based on the difference in sizes of the cations and the anions. Namely, when the voltage is applied the cations of the IL move into the anode and the anions move into the cathode of the actuator. Since the cations are larger than the anions, volume of the anode increases and volume of the cathode decreases. This causes the bending of the actuator towards the cathode [35]. The role of the SWNTs is indispensable in the actuator. Namely, due to the fact that the electrodes are volumetric networks in which the ions can penetrate, the number of uncompensated ions appearing in the electrodes as a result of the voltage applying turns out to be high enough to cause the bending.

The phenomena appearing in the systems comprising both ILs and SWNTs [31,32,35] inspired the author of the present dissertation to model theoretically one

more phenomenon of this type. The predicted phenomenon is described in the fifth chapter.

1.2 Theoretical study and computer simulation of liquids containing ions.

In the majority of theoretical works devoted to the study of electrolyte systems and also in many works on their computer simulation the so-called primitive model is used [36,37]. It is supposed in the model that likely charged ions of the electrolyte are spheres of the same size. The solvent in which the ions are moving is represented as a continuous structureless medium having the dielectric constant ε. For simplicity in some works this constant is assumed to be equal to unity [38]. If cations and anions are represented as spheres having the same diameter σ, the model is called "restricted primitive model" (RPM). If additionally the absolute charge values of the cations and the anions are supposed to be the same one has to do with the *symmetric* restricted primitive model [37]. Usually if in the literature nothing is mentioned about the cations and the anions absolute charges ratio the latter case is under consideration.

In the RPM a system is characterized by two reduced thermodynamic variables, namely, the temperature and the number density that are introduced via $T^* = kT\varepsilon\sigma/q^2$ and $\rho^* = \rho\sigma^3$. Here k is the Boltzmann's constant, T is the temperature, q is the absolute value of the ions charge, ρ is the concentration of ions.

Normally, in the works where the RPM is used for the description of electrolyte systems only electrostatic interactions of the charged particles and their excluded volume interactions are allowed for. The latter interactions are modeled by the hard spheres repulsion potential. Thus peculiarities of the Van der Waals interactions of the ions with the solvent molecules and with each other, as well as hydrogen bonds, are not taken into account. Although the RPM seems to be rather simple, a comprehensive commonly accepted theory of electrolyte systems in the

framework of RPM has not appeared yet [39]. Such a conclusion can be done if one examines the many different RPM based approaches [39-41].

The interest to the RPM that doesn't allow for peculiarities of particles interaction connected with their affinity has arisen after the appearance of the experimental work [42] which was later corroborated by the work [43]. In the work [42] a two component system consisting of the triethyl-*n*-hexylammonium thiethyl-*n*-hexylboride salt dissolved in diphenyl ether has been studied. It has been found that at room temperature the mixture segregates into two phases having different concentrations of the salt. When the mixture is heated the difference of the two phases becomes less pronounced and disappears when the temperature is approximately equal to 45 ^{0}C. Thus the two phases can be treated as the "liquid" and the "gaseous" states of the salt, while the ether can be treated as a medium with a fixed value of dielectric constant. The temperature 45 ^{0}C can be treated then as the "critical temperature" T_c of the salt.

Interest to the binary system was caused mostly by the fact that the difference of the two phases refractive indices Δn in the vicinity of the critical temperature T_c depends on temperature T as:

$$\Delta n \sim \left(T_c - T\right)^{1/2} \qquad\qquad 1.1$$

Thus it is described by the classical exponent $\beta \approx 1/2$. That's why a hypothesis has appeared that the long range Coulombic interactions determine the system's behavior. The fact is that it had been proven both theoretically and in experiment that a nonionic system's near critical behavior is Ising-like [40]. Namely in the case of a mixture of two nonionic substances the expression analogous to the expression 1.1 must comprise a different critical exponent β equal to ≈ 0.32.

The value of the parameter $u=q^2/\varepsilon kT\sigma$ has been calculated for the system studied in the work [42]. This parameter characterizes the ratio of the energies of electrostatic interactions and of thermal motion in the system. The value turned to

be equal to 15. That is about ten times higher than in other electrolytes, for example, the water based ones. The reason for that is the low dielectric constant of the diphenyl ether ($\varepsilon \sim 4$). That's why it has been concluded that electrostatic interactions have the key role in the system and they are the main reason of the phase segregation. This means that the RPM is appropriate for describing the system's behavior.

However it has been mentioned by the authors of the work [42] that the studied in the work system is more likely to be an exception. Normally for describing an electrolyte's behavior it is crucial to allow for peculiarities of the component species contact interactions [42]. This is the explanation of the divergence of results obtained in the work [42] and in the other experimental work [44] devoted to the same subject. To be more exact, in the work [44] the critical behavior of tetra-*n*-pentylammonium bromide aqueous solution near it's consolute point was studied. Behavior of this mixture is determined primarily by the hydrophobic effect that drives also the phase separation. Therefore the critical exponent value *β* for this mixture turned out to be equal to 0.319-0.337. That corresponds to the so-called Ising-like behavior.

According to the terminology that appeared in the domain of science connected with electrolyte systems, the mixtures investigated in the works [42] and [44] are representatives of the two different classes of the systems [45]. In the work [44] one of the so-called *solvophobic* systems has been studied. In solvophobic systems phase separation is principally driven by the same factor as in nonelectrolyte systems. Namely, by the "dislike" of the solute (an ionizable one in our case) for the solvent. In the vicinity of the critical point the solvophibic systems as well as nonionic systems exhibit the Ising-like behavior.

But the system investigated in the work [42] is one of the so-called *Coulombic* systems. Behavior of such systems is driven by electrostatic interactions. The RPM that doesn't allow for peculiarities of particles interaction is applicable to the

Coulombic systems. The critical exponent of Coulombic systems is classical, $\beta \approx 1/2$. An important characteristic of Coulombic systems is the fact that phase separation occurs in them at very low concentrations of ions. Let us note that in all the chapters of the present dissertation solvophobic systems are considered.

Theoretical and computer simulation studies of electrolyte systems within the framework of RPM have been primarily devoted to the determination of the critical temperatures and the critical ions concentrations and to the plotting of the systems coexistence curves.

When one tries to build the coexistence curve of a Coulombic system by means of computer simulation in the framework of the RPM the main obstacle occurs due to the fact that the curve is located in the region of low temperatures. At the low temperatures association of ions is significant and for this reason equilibration of the system happens to be very slow [46].

In the work [38] a Monte Carlo simulation of a Coulombic system in the framework of the RPM has been carried out. The technique used was the one described by the same authors in the paper [47]. The simulation cell was the surface of a four-dimensional sphere (hypersphere, for short), and the ensemble comprised 512 "ion pairs" each consisting of a cation and an anion located in opposite points of the hypersphere. The excluded volume interaction of the ion pairs were represented by the hard spheres repulsion potential, and electrostatic interaction w_{12} of two ion pairs was described by the so-called Coulomb-Schrödinger potential:

$$w_{12} = \frac{q^2}{R} \frac{\mathbf{z_1}\mathbf{z_2}}{\sqrt{1-\left(\mathbf{z_1}\mathbf{z_2}\right)^2}} \qquad\qquad 1.2$$

where R is the radius of the hypersphere, q – is the absolute value of an ions charge, and $\mathbf{z_1}$ and $\mathbf{z_2}$ are the unit vectors pointed from the center of the hypersphere to the cations of the two ion pairs.

The obtained in the work [38] coexistence curve (see Fig.2, *a)*) and the values of the critical temperature $T_c^* = 0.055\text{-}0.06$ and the critical ions volume fraction $\rho_c^* = 0.025\text{-}0.05$ do not coincide with the ones obtained in the work [37]. But in the work [37] a system consisting of only 32 ions was simulated. Besides the interaction of ions was represented there by means of the common Coulomb potential and the simulation cell was a simple cube with periodic boundary conditions. But application of the interaction potential decaying as $1/r$ in a system with periodic boundary conditions can lead to a significant error [38]. It has been proved that the
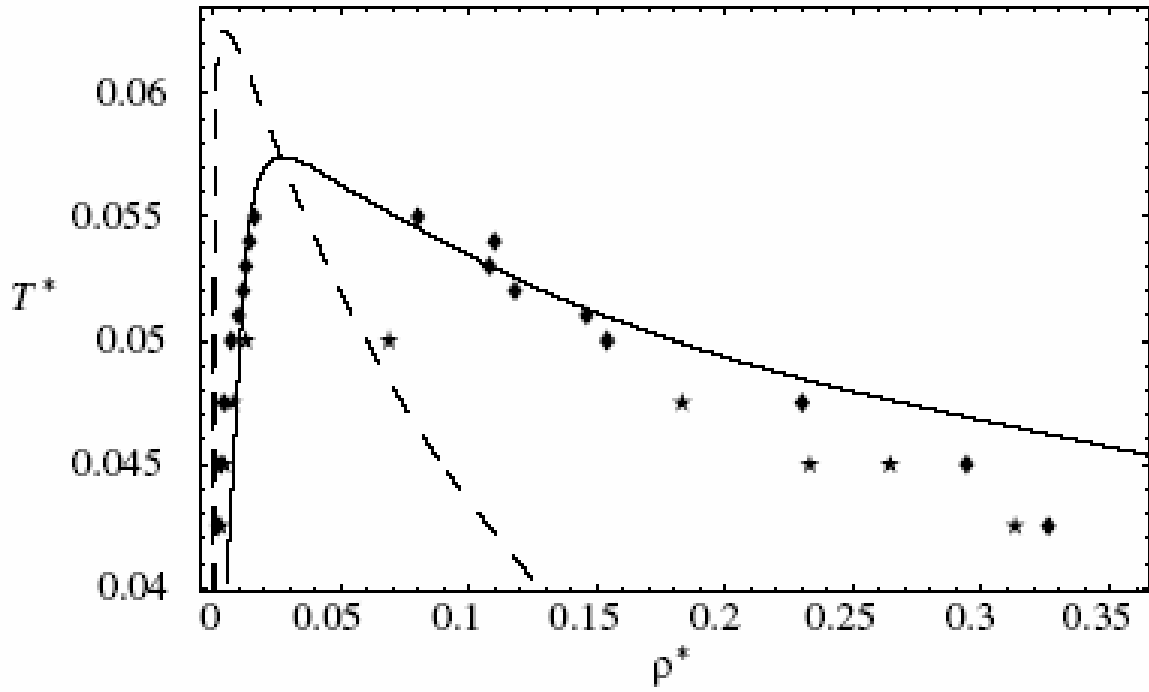

Figure 2. Built in the dimensionless variables coexistence curves of a Coulombic electrolyte system in the framework of the RPM obtained: (*a*) by means of computer simulation in the work [38] (diamonds), (*b*) by means of computer simulation in the work [46] (stars), (*c*) by means of calculation within the framework of the DH approach with taking into account the size of an ion [45] (dashed line) (*d*) by means of calculation within the framework of the DH approach with taking into account the size of an ion and also with allowing for the presence of strongly bound ion pairs that interact as dipoles with the surrounding medium of free ions (solid line) [45].   [36]

simulation on the surface of a four-dimensional sphere with utilization of the Coulomb-Schrödinger potential is just the way to get over the difficulty. Moreover the results of the work [38] roughly coincide with the results of the works [46,48] devoted to the same subject (see Fig.2, *b)*), although in the latter ones a different geometry of the simulation cell was used. Therefore the works [38,46,48] devoted to computer simulation of Coulombic electrolyte systems in the framework of the RPM are considered as more reliable.

Among the theoretical approaches to description of Coulombic electrolyte systems in the framework of the RPM the one should be first mentioned that is based on the Debye-Hückel (DH) theory. In the work [45] the coexistence curve has been built with the help of the DH theory. It has been allowed for therein in the solution of the Poisson-Boltzmann's equation that an ion is a sphere with a non-zero radius. The obtained in this way coexistence curve coincided qualitatively with the coexistence curves obtained in the works [38,46] (see Fig.2 *c)*). Moreover [45] it has been proved that the critical exponent of the system is classical. The calculated value of the critical temperature turned to be equal to $T_c^* = 0.0625$. That is almost equal to the one obtained in the computer simulation [38]. But the obtained value of the critical ions volume fraction turned to be equal to 0.005, that is more than five times less than the value obtained in computer simulation [38,46].

The authors of the work [45] supposed that the discrepancy is caused by the ability of the ions to couple into ion pairs. This leads to decrease of the concentration of free unassociated ions which take part in the electrostatic charge screening that drives the phase separation. Thus a higher total concentration of ions is required to produce a particular density of free ions for reaching the critical state. That's why the authors introduced in their model also strongly bound neutral ion pairs, that were represented as neutral particles diameter of which was assigned to be equal to $\sqrt{3}\sigma$, where σ is the diameter of an ion. The ratio of concentrations of the ion pairs and the

free ions was determined by means of the Bjerrum method (this approach was proposed earlier in the work [49]).

Namely, let Z_+, Z_-, and Z_{+-} be the internal partition functions of the free and paired ions, respectively. It is supposed that a chemical equilibrium exists between the free ions and the ion pairs and it is governed by the association constant $K(T) = Z_+Z_-/Z_{+-}$ equal to:

$$K(T) = 4\pi \int_{\sigma}^{R_{+-}} \exp(u\sigma/r)\, r^2 dr \qquad\qquad 1.3$$

where $u = q^2/k_B T \varepsilon \sigma$, and $R_{+-} = u\sigma/2$ [39]. The calculation next proceeds within the framework of the chemical model in imposing the equality of the chemical potentials $\mu_+ + \mu_- = \mu_{+-}$ between the free ions and the ion pairs. From this chemical equilibrium one deduces the fraction of free ions.

In the system modeled in this way phase separation and the critical state happened to be still possible. The calculated value of the critical temperature was the same as in the previous case and the calculated value of the critical ions volume fraction turned to be significantly higher and equal to 0.045 i.e. also roughly coinciding with the value obtained by means of computer simulation. But generally the new phase diagram differed significantly from the phase diagrams obtained by means of computer simulation in the works [38,46]. Moreover the phase diagram looked unreliable because it admitted emerging of the "liquid" (the phase with the higher concentration of ions) in the "gas" (the phase with the lower concentration of ions) in the course of isochoric heating.

To get rid of the new calculations disadvantage the authors [45] took into account that although an ion pair is as a whole neutral it possesses a dipole moment. And the effect of the electrostatic field produced by ion pairs should also be allowed for especially in the case when the concentration of free ions is low, i.e. at low total concentrations of ions and at low temperature. (The phase diagram built without

taking this effect into account has the strange peculiarity right in this region.) That's why one more additive to the free energy of the system has been calculated in the framework of the DH approach. This additive arises due to interaction of ion pairs represented as spheres having a dipole moment and the surrounding them gas composed of free ions. The contributions to the free energy caused by interaction of a higher order multipoles have not been allowed for by the authors because according to their estimates influence of these terms on the system's behavior is insignificant.

The obtained eventually coexistence curve and (see Fig.2 *d)*) the values of the critical temperature $T_c^* = 0.057$ and the critical ions volume fraction $\rho_c^* = 0.028$ coincide well with the results of the computer simulation in the works [38,46]. The Fisher-Levin theory of phase separation in Coulombic electrolyte systems presented in the paper [45] and named after the authors of the work is accepted as the most successful one [36,50].

In the two subsequent works [51,52] devoted to the RPM computer simulation of Coulombic electrolyte systems the distortions have been thoroughly taken into account that arise due to finiteness of the simulation cell, and somewhat different values of the critical temperature $T_c^* = 0.049$ and the critical ions volume fraction $\rho_c^* = 0.07 - 0.08$ have been obtained. The possible explanation is that the Fisher-Levin theory is a mean field theory, and for this reason it is not well applicable in the vicinity of the critical point, where fluctuations play a significant role. However in the region far from the critical point the coexistence curve obtained in the work [51] anyway coincides well with the one obtained by Fisher and Levin.

In subsequent theoretical works [39] and [50] an attempt has been made to develop further the Fisher-Levin theory by means of taking into account also dipole-dipole interactions. However the derived in these works critical ions volume fraction happened to be even less than in the work [45]. Thus the obtained therein results fit

even worse with the computer experiment results [38,46,51] than the ones obtained by means of the original Fisher-Levin theory.

In the theoretical work [36] the liquid-gas phase boundary in a Coulombic system has been studied in the framework of RPM. The near-boundary ions concentration profiles and the surface tension of the boundary have been calculated at different values of temperature. The calculations have been carried out in the framework of the Fisher-Levin approach. To account for the contribution of components concentrations inhomogeneities near the boundary the expansion of the system's free energy in powers of the ions concentration gradient has been carried out in the work [36]. The expansion has been truncated after the square-gradient term. This can be done only if the concentrations gradients are not too large. Thus, the results of the study are reliable only not far from the critical point.

On the other hand, as it has been already mentioned, the used in the calculations Fisher-Levin theory is not well applicable in the vicinity of the critical temperature T_c. For this reason, authors of the work [36] pretend to a reliability of their results only in the case if the temperature T of the system under investigation lies in the interval $0.85 < T/T_c < 0.95$. One can see from the figures representing the calculation results of the work [36] that the thickness of the transition layer between the two phases (the thickness of the phase boundary) is at $T/T_c = 0.8$ of order of several ion diameters and it increases only when the system's temperature T becomes very close to the critical one.

This is in agreement with the results described in the third chapter of the present dissertation where a solvophibic two-component electrolyte system is considered. Approaching of the system to the critical state is modeled there by the decrease of the parameter $\tilde{\chi}$ and it's approaching to the threshold value of $\tilde{\chi}^*$, when the mixture turns into a homogeneous one.

Since a Coulombic system has been considered in the work [36] an asymmetry in interaction of cations and anions with the neutral molecules has not

been taken there into account. In contrast to the approach described in the third chapter of the present dissertation such an approach implies that concentrations of cations and anions are equal in any point of the mixture, and therefore formation of an electrostatic double layer at the interface is impossible.

In this respect the approach presented in the third chapter is more close to the one in the theoretical work [53] of Onuki, where distribution of a salt's ions in a biphasic system has been studied. It has been allowed for by Onuki that cations and anions interact with the different phases in a different way (i.e. the system has been modeled as a solvophibic one). Thereto solvation chemical potentials of the cations and the anions in both of the phases were introduced. The concentration profiles of the ions in the near-boundary layer have been calculated and it has been demonstrated that equality of the cations and the anions concentrations in the vicinity of the phase boundary is broken if there exists a difference of their solvation chemical potentials in the two phases. This means that an electrostatic double layer appears at the phase boundary. That causes the emergence of the potentials difference between the two phases (the one known in electrochemistry as the Galvani potential difference [53]).

Besides it has been demonstrated in the work [53] that the surface tension of the phase boundary increases with the increase of the average salt concentration in the system and the mixture's critical temperature (the temperature at which the mixture turns into a homogeneous one) depends significantly on the salt concentration. The fundamental distinction between the system studied in the work [53] and the system studied in the third chapter of the present dissertation lies in the concentrations of ions. Namely, in the system modeled by Onuki the concentration of ions is supposed to be very low while in the third chapter of the present work a system is studied in which one of the phases (an IL) is composed almost entirely of ions.

In the last four years Onuki published also three interesting theoretical works [54-56] based on the Ginzburg-Landau theory which are devoted to phenomena connected with solvation of ions in various media. In the work [54] behavior of a gas composed of polar molecules near an ion has been studied. It has been proved that near an ion a drop of liquid is formed and it's size has been calculated. (For the first time this phenomenon was observed by Wilson more than hundred years ago). Thus in the work [54] both effects of electrostriction and of polarization alignment of gas molecules near the ion have been allowed for to describe the solvation of the ion.

In the work [55] a theory has been built describing solvation of an ion in a near-critical binary mixture of two polar liquids. In the work [56] solvation of an ion in a liquid crystal has been studied. It has been shown therein that the ion's electrostatic field violates orientation of the liquid crystal on a large scale as compared with the size of the.

The theoretically proved in the work [53] effect of phase boundary surface tension growth with the growth of an ionic admixture concentration had been observed in experiment already long before [57]. For example, the work [58] is one of the recent experimental works devoted to this subject. The phenomenon has been attracting the interest of researchers for a long time already. The fact is that there exists an opposite much better known effect of an admixture small concentration on the surface tension of a phase boundary. Namely, when a surfactant is added to a biphasic system, the surface tension of the phase boundary decreases.

The excess of admixture at a gas-liquid interface can be determined as:

$$\Gamma = \int\limits_{0}^{\infty} \left[c(z) - c_b \right] dz \qquad\qquad 1.4$$

where integral is taken over the coordinate z, perpendicular to the interface and pointed in the direction of the liquid, $c(z)$ is the concentration of the admixture at the distance z from the interface, and c_b is the admixture's concentration in the liquid far

from the interface. Then the following relation obtained from the Gibbs-Duhem equation must be valid [59]:

$$\left(\frac{d\gamma}{d\mu}\right)_{T,V} = -\Gamma \qquad\qquad 1.5$$

where μ is the chemical potential of the admixture and γ is the surface tension of the phase boundary.

If an admixture is surface active its concentrating at the interface is favorable: $\Gamma > 0$. Thermodynamic stability requires that the chemical potential of a system's component grows when its concentration increases: $d\mu/dc > 0$. Thus, it follows from the eq. 1.5 that an increase of the average surfactant concentration in the system (or at the phase boundary, what is equivalent) must lead to a decrease of the surface tension of the phase boundary: $d\gamma/dc < 0$.

Vice versa, if the surface tension increases when the average concentration of an admixture in the biphasic system is increased, then, as it follows from the eq. 1.5, the concentration of this admixture near the interface must be less than in the bulk of the liquid phase: $\Gamma < 0$ [59].

Onsager and Samaras published in the year 1934 one of the first theoretical works [60] where it was demonstrated that concentration of an ionic admixture at a liquid's surface adjacent to a gas is less than in the bulk of the liquid far from the surface, and the surface tension of this phase boundary increases with growth of the admixture's concentration in the liquid. In the Onsager-Samaras (OS) model the system is represented as a plane separating a medium with dielectric constant equal to unity (gas) and a medium with a fixed dielectric constant (liquid) containing ions. In such a system decrease of the ions concentration near the interface as compared to the bulk of the liquid appears due to the dielectric constant discontinuity at the phase boundary. Namely, electrostatic field of an ion polarizes the boundary and induces on it a charge of the sign similar to that of the ion. This induced charge repels the ion. The calculations of Onsager and Samaras were also based on the DH theory.

The results obtained by means of the OS approach are in good agreement with experiment at concentrations of ions in the system less than 0.1 mole/liter. According to the calculations based on this approach the characteristic thickness of the near-surface layer where concentration of ions is less than in the bulk of the liquid is of the same order of magnitude as the Debye radius, reciprocal of which is expressed as $\kappa = [8\pi c_b z^2 e^2/\varepsilon k_B T]^{1/2}$, where ε is the dielectric constant of the liquid, e is the elementary charge, and ze is the charge of an ion. The change of the phase boundary surface tension caused by the ionic admixture in the limit of very low ions concentrations is equal to:

$$\Delta\gamma = c_b k_B T l_b \left[-\ln\frac{\kappa l_b}{2} - 2\gamma_E + \frac{3}{2} \right] \qquad 1.6$$

where $l_b = e^2/\varepsilon k_B T$ is the Bjerrum length and $\gamma_E = 0.5772$.

Not long ago the OS approach was further developed in the theoretical work [57] predictions of which are in agreement with experimental data concerning NaCl solutions [58] up to ions concentration of 1 mole/liter. It has been additionally taken into account in the work [57] that solvate shells are formed around an ion. These solvate shells don't allow the ions to be closer to the surface of the liquid than the distance equal to the thickness of the shells. This leads to an extra increase of the surface tension.

In the work [61] the proposed in the work [57] model was generalized for the case of an asymmetric electrolyte, namely, an electrolyte comprising the so-called multivalent ions. This means that in this electrolyte ratio of oppositely charged ions amounts is not equal to unity. Several counterions fall to the share of each multivalent ion. This number is the so-called valence of the multivalent ion. Results of the calculations carried out in the work [61] are in excellent agreement with the results of the measurement carried out in the work [58] for the case of a $MgCl_2$ solution. However, in the model proposed in the work [61] the thickness of the near-surface layer of liquid where ions can't enter because of their solvate shells is not an

a priori fixed parameter. Value of this parameter has not been calculated by the authors on basis of experimental data concerning structure of the solvate shells. It has been just chosen to provide the best coincidence of the calculations results and the experimental data [58] concerning the surface tension.

Let us also briefly mention here our work [62], in which distribution of an asymmetric electrolyte in a porous polyelectrolyte gel has been studied. It has been shown therein by means of simple entropy and electrostatic field energy estimates that the ratio of the multivalent ions concentrations in the pores and in the network of the gel increases dramatically with increase of the multivalent ions valence.

Another attempt to generalize the OS theory has appeared in literature almost simultaneously with the work [57]. Namely, in the work [63] it has been taken into account that a cation and an anion possess different polarizabilities. The ability of an ion to be polarized originates an additive to his potential in the field produced by the charge induced on the phase boundary by the very ion. Hence, such a break in the symmetry of the oppositely charged ions leads to the inequality of their concentrations near the phase boundary. This means that at the interface an electrostatic double layer arises. That causes the origination of one more additive to the ions potential. Since the introduced in the model complication doesn't allow an analytical treatment the system has been studied by the authors [63] numerically. It has been proved that polarazabilities of ions also exert a significant influence on the phase boundary surface tension.

In the work [59] the effect of a solvent droplet surface tension growth with the increase of an admixture concentration (including an ionic admixture) has been analyzed theoretically and demonstrated by means of computer simulation on basis of a more general assumption. Namely, it has been supposed that energy of an admixture molecule attraction to a molecule of the solvent is higher than the energy of two solvent molecules attraction. For this reason the total interaction energy of the mixture's molecules is less if a given admixture molecule is in the bulk of the

29

solvent than if it is near the phase boundary (because in the bulk the admixture molecule screens a larger number of contacts between the solvent molecules which are less energetically favorable than contacts of this molecule with the solvent molecules). Thus the admixture molecules are drawn into the bulk of the solvent and their concentration therein is higher than near the phase boundary. This causes the decrease in the surface tension with the increase of the average admixture concentration.

In the work [64] the effect of a solution/gas interface surface tension growth with the increase of an ionic admixture concentration in the solution has been studied by means of a Monte Carlo computer simulation. To avoid possible problems related to the finiteness of the simulation cell an entire drop of liquid has been simulated. The solution was modeled as a Coulombic electrolyte system in the framework of the RPM. Electrostatic interactions of the ions have been calculated on each step directly by means of solving the Poisson equation.

The advantage of an RPM based computer simulation of a Coulombic system over its RPM based OS analytical treatment lies in the fact that the former has no limitations connected with possible values of the ions concentration, while the latter is applicable only at low ions concentrations at which the DH approach is valid. As to the solvate shells of ions, their presence can be allowed for in the computer simulation just by means of specifying a larger radius of the ions.

In the work [64] it has been demonstrated that the excess amount of ions Γ at the surface of a liquid drop and the surface tension are proportional to the ions average concentration in the drop. The computer simulation results coincide with the OS theory predictions at low concentrations of ions, and they are in agreement with the experimental results up to ions concentrations of order 1 mole/liter [64]. Besides, it has been found out in the work [64] that the thickness of the solution near-surface ions depleted layer is roughly three times larger than an ion's diameter. This is in

agreement with the results concerning the thickness of the phase boundary transition zone that have been obtained in the third chapter of the present dissertation.

Computer simulation of a liquid-vapour phase boundary has been carried out also for the case of an IL. In the work [65] by means of the Monte Carlo and molecular dynamics methods it has been demonstrated in the framework of RPM that the surface of an IL is rather rough and has a larger thickness than interfaces of simple liquids and water (especially at the temperature close to the critical one); and in the bulk of the IL cavities that have size of several ion diameters can be spontaneously formed. It has been also demonstrated in the work [65] that surface tension of the ionic interface is much higher than that of simple fluids, and of the same order of magnitude as the water surface tension, that is in agreement [65] with experimental data despite the simplicity of the RPM.

To conclude the review of theoretical works devoted to study of ion containing systems, let us mention the papers in which a Flory-Huggins type lattice approach has been used for explaining the properties of ILs. The works [26] and [66] are experimental in the first place. Therein macrophase separation of the mixtures IL/nIL has been investigated. In order to explain the experimentally obtained phase diagrams some calculations on basis of the Flory-Huggins approach have been carried out. The obtained by means of these calculations phase diagrams coincided well with the ones obtained in experiment.

Let us note here that the models of IL/nIL mixtures described in the chapters 2,3,4 of the present dissertation are also based on the Flory-Huggins approach. However the latter have almost nothing to do with the considerations proposed in the works [26] and [66]. The fact is that in the models proposed in these works a base unit of an IL is represented as a single molecular entity. In other words, it is supposed that all ions of the IL form strongly bound neutral ion pairs. Thus in this theoretical treatment it is just not taken into account that an IL is actually composed of ions. Vice versa, in the models proposed in the present dissertation [16,19,20] the

31

fact that an IL consists of ions that are not strongly bound to each other is of primary importance.

It is supposed in the works [26] and [66] that a "molecule" of the IL is larger than a molecule of the nonionic solvent. To allow for this fact it is supposed that an IL molecule is a polymer molecule that consists of monomer units having the same size as the molecules of the nonionic solvent. This assumption is rather debatable. But it allows applying of the Flory-Huggins theory expressions describing the free energy of a polymer solution to the modeled system. The coincidence of the experimental and the theoretical curves is achieved in the works [26] and [66] by means of choosing the optimal values of an IL "molecule" "degree of polymerization" and of the Flory-Huggins parameter characterizing the IL "molecule" interaction with a molecule of the nonionic solvent. The obtained thus in the work [66] ratio of the IL's cation and anion total volume to the volume of a nonionic solvent molecule for the $(BMI)BF_4$ + water system happened to be two times smaller than the actual ratio.

2. Explanation of the high solvent power of ionic liquids.

In the present chapter [16] a mixture of an ionic liquid and a normal nonionic solvent is considered. The goal of the consideration is the determination of the conditions under which the mixture is homogeneous. Main subject of the investigation is the influence of the Van der Waals interactions of the IL's cations with the IL's anions and of the ions with the molecules of the nonionic solvent on the IL's solvent power.

Cations and anions are considered as individual components of the mixture which is represented thus as a ternary one, i.e. consisting of cations, anions and neutral molecules. Formation of ion pairs is not taken into account for the sake of simplicity. Allowing for this effect would not change the obtained results qualitatively.

The following qualitative explanation of the high solvent power of ILs can be proposed. Let us imagine that the contact of an IL's cation and an IL's anion is energetically very unfavorable or, in other words, they are strongly incompatible. Theoretically, if these particles lost their charge but their Van der Waals interactions stayed the same then a homogenous mixture of these particles could not exist, and phase separation would necessarily occur. But since the cations and the anions are in fact oppositely charged their segregation is impossible since it would originate an electrostatic field with a very high energy. That's why they are homogeneously mixed.

Now let us imagine that the energies of a solute molecule contacts with a cation and an anion of the IL are much less than their mutual contact energy. If such a molecule is inserted in the bulk of the IL several energetically unfavorable contacts of cations and anions disappear and they are replaced by more energetically favorable contacts of the molecule and the surrounding ions. On the other hand, when the neutral solute molecules appear in the bulk of the IL the IL's cations and

anions remain homogeneously mixed in the solution, hence, average electrostatic charge remains equal to zero in any point of the mixture and no extra energy of electrostatic field arises.

Thus dissolution of such neutral molecules in the IL turns out to be energetically favorable. Generally, solvent power of an IL increases with the growth of the incompatibility of its cations with its anions. As to possible formation of ion pairs, their appearance would decrease the total number of "active" ions in the IL and hence would decrease its solvent power, but it would not change qualitatively the dependence of the solvent power on the character of the IL's cations and anions Van der Waals interaction. This reasoning can be supported in the following way by analytical derivation.

Let us consider a homogeneous mixture IL/nIL. For definiteness, let us assume that cations and anions of the IL and neutral molecules of the nIL are of the same size. It needs no saying that it is not the case in real systems. It is well known, for example, that the most popular as an object of scientific study imidazolium ILs (like $(BMI)BF_4$) are composed of a cation and an anion that have significantly different sizes. However, difference in the mixture components molecules sizes is also not the major factor of the predicted here phenomenon. The allowing for of this difference would introduce significant complication in the theoretical treatment but it would not change qualitatively the main prediction of the theory.

To describe the system we use a lattice model. It is supposed that the whole volume of the mixture is composed of identical elementary cubic cells and each of the cells contains one molecule of a component of the mixture. Each molecule of the system is located strictly within the bounds of one of the cells. Since it is supposed that there are no empty cells it is allowed for in the model that not a gas but an uncompressible mixture is considered. The mixture's entropy is determined by means of counting the number of different arrangements of the components molecules set over the set of the elementary cells.

To each couple of molecules located in adjacent cells the contact energy is assigned which is determined by the types of the two molecules, and sum of all the energies of the contacts in the system is calculated to obtain the total Van der Waals interactions energy. To characterize quantitatively mutual contacts energies of different components molecules corresponding Flory-Huggins parameters are introduced. In the case under consideration there are three types of contacts: cation – anion, cation – neutral molecule, anion – neutral molecule. They are described by the parameters χ_{+-}, χ_{+}, χ_{-} (see fig. 3.), respectively. The larger is the value of a Flory-Huggins parameter the less energetically favorable is the corresponding molecules contact. (Meaning of the parameter $\tilde{\chi}$ presented in the figure 3 is explained in the next chapter.)

Let us note here that according to the terminology used in theoretical works devoted to study of electrolyte systems the used in the present chapter model can be
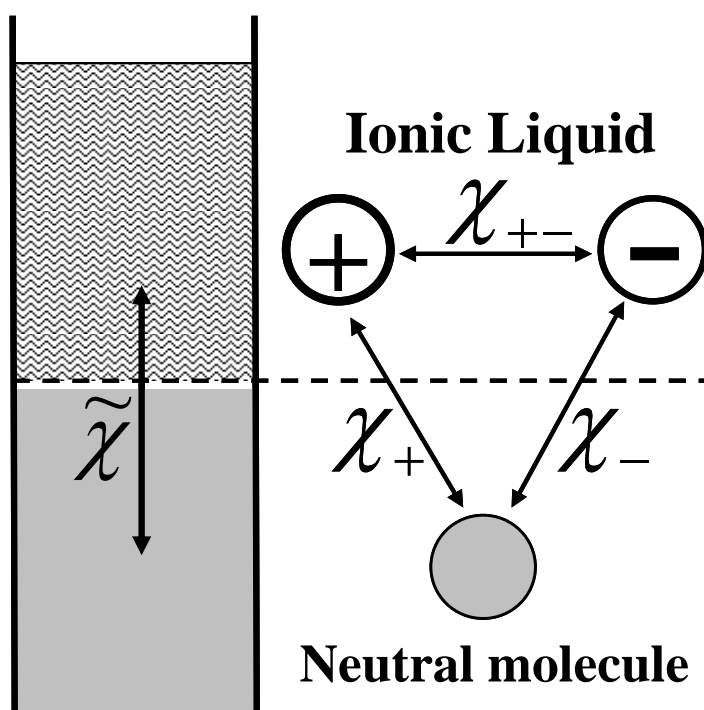

Figure 3. Schematic diagram representing parameters used for the description of the Van der Waals interactions in the system.

termed as a symmetric restricted primitive model *on a lattice*. The system described by the model is of no doubt a solvophobic one.

Let Φ_+ and Φ_- be the volume fractions in the solution of the IL's cations and the IL's anions, respectively. The unoccupied by the ions space of the mixture is occupied by nonionic liquid and volume fraction of the latter in the mixture is, hence, equal to *1-Φ_+-Φ_-*. The normalized to the number of elementary lattice cells entropic contribution f_{ent} to the free energy of the system caused by translational motion of the cations, the anions, and the neutral molecules is equal to:

$$f_{ent}/kT = \Phi_+ \ln \Phi_+ + \Phi_- \ln \Phi_- + (1 - \Phi_+ - \Phi_-)\ln(1 - \Phi_+ - \Phi_-) \qquad 2.1$$

The normalized to the number of elementary lattice cells contribution f_{int} to the free energy caused by Van der Waals interactions of the molecules is equal to:

$$f_{int}/kT = \chi_{+-}\Phi_+\Phi_- + \chi_+\Phi_+(1 - \Phi_+ - \Phi_-) + \chi_-\Phi_-(1 - \Phi_+ - \Phi_-) \qquad 2.2$$

The characterizing contact of two molecules of the types A and B parameter χ_{AB} is equal to:

$$\chi_{AB} = 6\left(E^{AB} - \frac{E^{AA} + E^{BB}}{2} \right)/kT \qquad 2.3$$

where E^{AB}, E^{AA}, and E^{BB} are the contact energies of the located in the adjacent cells molecules of the types A and B, A and A, and B and B, respectively. These values can be determined by means of the molecules interaction computer simulation [67].

The formula 2.2 is a special case of the general expression describing the contribution to a mixture's free energy caused by its molecules Van der Waals interactions for the case when the mixture is not spatially homogeneous. Derivation of that expression is given in the appendix 1.

Since a spatially homogeneous solution is considered, concentrations of the cations and of the anions in all its points are equal to each other, and, hence, electrostatic charge is equal to zero in all the points and the energy of electrostatic field is equal to zero. The contribution to the electrostatic free energy caused by the ions concentrations fluctuations is also not taken into account while its influence on

the predicted phenomenon is negligible. Nevertheless the fact that the system is ionic plays implicitly the key role in the present theoretical treatment. Namely, opposite charges of the cations and the anions are the very reason of why the concentrations of the cations and the anions are equal in al the points of the solution.

From the equality of the concentrations and from the assumption of the equality in sizes of the cations and the anions it follows that their volume fractions in the homogeneous solution must be equal to:

$$\Phi_+ = \Phi_- = \Phi/2 \qquad\qquad 2.4$$

where Φ is the volume fraction of the entire IL in the mixture. The total free energy of the system normalized to the number of elementary lattice cells is equal to the sum of the equations 2.1 and 2.2. With taking into account the equation 2.4 it can be written as:

$$\frac{f}{kT} = \Phi \ln \frac{\Phi}{2} + \chi_{+-} \frac{\Phi^2}{4} + (1 - \Phi) \ln (1 - \Phi) + \chi (1 - \Phi) \Phi \qquad 2.5$$

where χ is the average parameter describing simultaneously both interactions of the cations and the anions of the IL with the neutral solute molecules:

$$\chi = \frac{(\chi_- + \chi_+)}{2} \qquad\qquad 2.6$$

As a matter of fact, χ is the parameter characterizing interaction of a solute molecule and an IL molecule consisting of two ions.

If one knows the expression of a mixture's free energy one can obtain the equation describing the spinodal of the mixture's macrophase separation by means of equating the second derivative of the free energy to zero: $\partial^2 f / \partial \Phi^2 = 0$ [68]. After applying this procedure to the expression 2.5 one obtains:

$$\chi = \frac{1}{2\Phi (1 - \Phi)} + \frac{\chi_{+-}}{4} \qquad\qquad 2.7$$

The dependence 2.7 of the parameter χ on the volume fraction Φ of the IL in the mixture is represented in the figure 4 (curve *a)*). The value of the parameter χ_{+-}

is taken in this case to be equal to 12. The figure 4 is the phase diagram of the mixture IL/nIL. It has the following physical meaning. If the system is described by the couple of parameters (Φ, χ) which correspond to a point located over the curve *a)* then such a mixture would be unstable in the homogeneous state. In this case the mixture must segregate into two macrophases. But if the point with coordinates (Φ, χ) is located below the curve *a)*, then the corresponding to this point homogeneous mixture IL/nIL is stable.

In general, the last condition is not the sufficient one to ensure the homogeneous mixture's stability. A homogeneous mixture is absolutely stable if the value of the system's free energy is equal to its absolute minimum. This condition is fulfilled if the point (Φ, χ) is below the binodal curve which is located somewhat lower than the spinodal curve. However, if we treated the binodal curve instead of the spinodal curve as the boundary of the phase separation domain our analytical
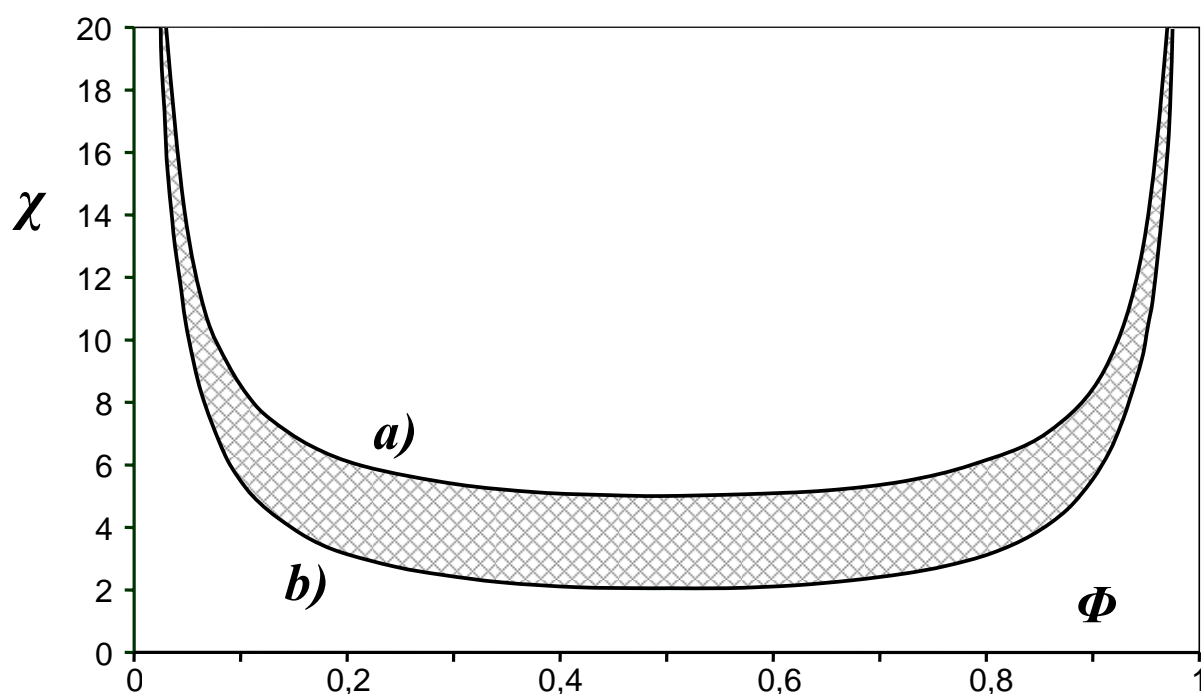
Figure 4. Spinodal of the mixture IL/nIL macrophase separation at the value of the parameter χ_{+-} equal to 12 (*a*), and the spinodal of macrophase separation of the mixture of the same nIL and a nonionic solvent equivalent to the IL (*b*).

treatment would become a bit more complicated, but the main result of our speculations would stay the same. The binodal of the mixture is considered in the next chapter.

For comparison, let us consider a mixture of two normal nonionic liquids molecules of which are also of the same size. Let us denote the volume fraction of one of the components again as Φ and the Flory-Huggins parameter characterizing interaction of the two components molecules again as χ.

The normalized to the total number of elementary lattice cells free energy f_0 of this two-components system can be expressed as:

$$f_0/kT = \Phi \ln \Phi + (1 - \Phi)\ln(1 - \Phi) + \chi(1 - \Phi)\Phi \qquad 2.8$$

where the first two terms represent the entropic contribution to the system's free energy which is caused by the translational motion of the two components molecules and the last term represents the contribution caused by the molecules interactions.

After equating again to zero the second derivative of the describing the free energy expression one can obtain the following equation which describes the mixture's macrophase separation spinodal:

$$\chi = \frac{1}{2\Phi(1 - \Phi)} \qquad 2.9$$

This dependence is also presented in the figure 4 by the curve *b)* which is located lower than the curve *a)*.

Thus, if at any given ratio of two mixed components concentrations one starts at a high value of χ and decreases it (on the phase diagram this corresponds to the motion downwards from a point located in the upper part) then in the both considered cases the mixture from a heterogeneous one turns into a homogeneous one as the point representing the system's state passes the corresponding spinodal curve. But the homogeneous mixture of an IL and a nIL is formed earlier than the homogeneous mixture of the same nIL and a nonionic solvent equivalent to the IL. (According to our definition, equivalence of two solvents with respect to a solute

means that the Flory-Huggins parameters characterizing interactions of the both solvents molecules with the solute molecules are the same.)

The IL "extra solvent power domain" is shaded on the phase diagram presented in the figure 4. The width of this domain, i.e. the distance between its boundaries along the χ coordinate axis is equal to $\chi_{+-}/4$. (Compare the equations 2.7 and 2.9). Thus, it has been proven that the stronger is the incompatibility between cations and anions of an IL the higher is the solvent power of the IL with respect to an arbitrary solute.

In conclusion of the present chapter let us mention a possible erroneous deduction concerning the preceding argumentation. Namely, the argumentation is formally valid for any equimolar mixture of two nonionic components A and B acting as a binary co-solvent for a third nonionic liquid. According to the same argumentation if the parameter χ_{AB} which describes the interaction of the A and B components is positive their equimolar mixture is also to have some extra solvent power and it is not clear what the unique role of an IL is.

The answer to this objection is the following. As a matter of fact such a two components AB solvent can exist only if the two components do not segregate. This is possible only if the value of the parameter χ_{AB} is less than 2. That follows from the equation 2.9, if one substitutes in it the values of the components volume fractions, which are in this case equal to 0.5. Thus, for this AB co-solvent the boundary of the homogeneous state domain on the phase diagram of its mixture with a nIL (similar to the curve *a)* in the figure 4) can be higher than the boundary for the case of a normal one-component solvent (curve *b)*) not more than by $\chi_{AB}/4 = 0.5$.

But in the case if an IL is the solvent, there are no such limitations of the extra solvent power caused by the cations and the anions incompatibility, since, as it has been already mentioned, segregation of oppositely charged ions is impossible. The maximal value of $\chi_{+-}/4$ in this case is limited only by the maximal cations and anions incompatibility that is generally possible in nature.

Let us summarize briefly the chapter 2. It has been demonstrated that the higher is the energy of an IL's cation and anion contact caused by their Van der Waals interaction, i.e. the stronger is their incompatibility, the stronger is the solvent power of this IL with respect to an arbitrary nonionic liquid.

3. Study of the phase boundary between an ionic liquid and a nonionic liquid.

In this chapter the study of a macroscopically phase separated mixture of an ionic liquid and a normal nonionic solvent [19] is presented. The subject of the study is the interface between the two phases. Namely, the components concentrations profiles near the interface, surface tension of the interface, and the thickness of the transition region between the two phases are determined. As in the previous chapter the investigation is focused on the influence of the components Van der Waals interactions on the system's properties. The lattice model with the same main assumptions as in the previous chapter and with the same notation of parameters characterizing the mixture's components Van der Waals interactions (see the figure 3 and the equation 2.6) is used.

3.1 Binodal of the studied mixture.

A flat phase boundary is considered. Hence, the problem is one-dimensional and the components concentrations vary only along one coordinate perpendicular to the boundary. Let us denote the coordinate by x. The concentrations gradient is present only in the transition region at the interface. On the both sides far from the interface concentrations of the cations and the anions of the IL must be equal, otherwise electrostatic field having infinite energy would arise. That's why far from the interface the mixture's free energy f per one elementary lattice cell is expressed by the equation 2.5.

Concentrations of the IL far from the phase boundary can be determined with the help of the phase equilibrium condition. Namely, chemical potentials of each component in the two phases and osmotic pressures must be equated:

$$\frac{\partial f}{\partial \Phi}\bigg|_{\Phi_{-\infty}} = \frac{\partial f}{\partial \Phi}\bigg|_{\Phi_{+\infty}} \qquad \left(\Phi\frac{\partial f}{\partial \Phi} - f\right)\bigg|_{\Phi_{+\infty}} = \left(\Phi\frac{\partial f}{\partial \Phi} - f\right)\bigg|_{\Phi_{-\infty}} \qquad 3.1$$

where as $\Phi_{+\infty}$ and $\Phi_{-\infty}$ the sought volume fractions of the IL on the both sides far from the phase boundary are denoted. The system of equations 3.1 can be

simplified. If one adds to f the linear in $\varPhi$ term $\varPhi(\ln2 - \chi_{+-}/4)$ one obtains the value f_{symm} which is described by expression that is invariant with respect to substitution of $1- \varPhi$ for $\varPhi$ and vice versa:

$$f_{symm} = \varPhi\ln(\varPhi) + (1-\varPhi)\ln(1-\varPhi) - \chi_{+-}\frac{\varPhi(1-\varPhi)}{4} + \chi\varPhi(1-\varPhi) \qquad 3.2$$

Terms of f which are linear in $\varPhi$ are cancelled when f is substituted in the system of equations 3.1. That's why in order to get the sought values $\varPhi_{+\infty}$ and $\varPhi_{-\infty}$ the value f_{symm} can be substituted in the system 3.1 instead of the value f.

As a matter of fact, the system of equations 3.1 solution is the finding of the two points of the representing the function $f(\varPhi)$ curve, which have a common tangent. The function $f_{symm}(\varPhi)$ has on the segment [0,1] either two inflections and two minima in the points symmetrical with respect to the value of $\varPhi = 0.5$ or only one minimum in the point $\varPhi = 0.5$. This depends on the values of the Flory-Huggins parameters characterizing the system. Since the function is symmetrical with respect to the value of $\varPhi = 0.5$, if its tangents in two different points coincide, then this common tangent must be horizontal. Therefore, the solution of the system of equations 3.1 with f_{symm} substituted for f is equivalent to the solution of one simple equation:

$$\frac{\partial f_{symm}}{\partial \varPhi} = 0 : \qquad \ln\varPhi - \ln(1-\varPhi) + (1-2\varPhi)\widetilde{\chi} = 0 \qquad 3.3$$

The equation 3.3 can have two sought solutions $\varPhi_{+\infty}$ and $\varPhi_{-\infty} = 1- \varPhi_{+\infty}$, and it always has the root $\varPhi = 0.5$, that has no physical meaning. In the expression 3.3 the following parameter has been introduced:

$$\widetilde{\chi} = \chi - \chi_{+-}/4 = \frac{\chi_+ + \chi_-}{2} - \chi_{+-}/4 \qquad 3.4$$

$\widetilde{\chi}$ is the only one parameter determining the macrophase behavior of the system. Namely, it determines whether the mixture is homogeneous, and in the case if the mixture segregates in two phases, this parameter determines the compositions of the two phases. Generally, when one has to do with macrophase separation only, if concentrations of the cations and the anions of an IL are equal in all the points

of the system, the IL is equivalent to the solvent interaction of which with the given solute is characterized by the Flory-Huggins parameter $\widetilde{\chi}$.

The solution of the equation 3.3 (the binodal curve) is presented in the figure 5 (curve *a)*). This is a phase diagram having the following physical meaning. If in the considered mixture the average volume fraction Φ of IL is such that the point with coordinates $(\Phi, \widetilde{\chi})$ is located below the binodal curve then the spatially homogeneous state of the mixture is stable. But if the point is located over the curve, then the homogeneous mixture is not stable, and when it segregates, the volume fractions of the IL in the two emerging phases are equal to the abscissa coordinates of the points where the horizontal line with the ordinate $\widetilde{\chi}$ intersects the binodal curve.

For comparison, the spinodal of the mixture IL/nIL considered in the previous chapter is also presented in the figure 5 (curve *b)*). As in the present
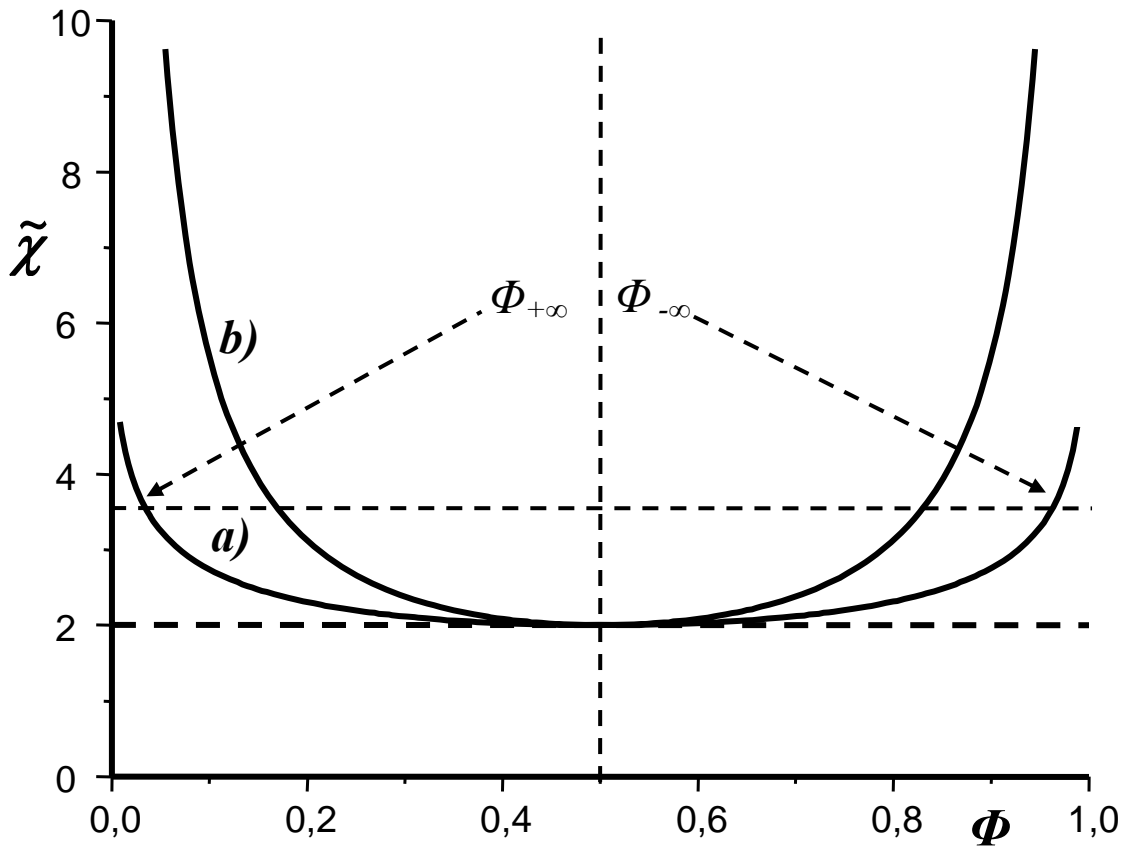

Figure 5. Binodal (*a*) and spinodal (*b*) curves of the mixture IL/nIL macrophase separation in the coordinates $\widetilde{\chi}$, Φ.

chapter a phase boundary is considered it is implied that the studied system is characterized by the point on the phase diagram (figure 5) that is located in the phase separation domain, i.e. over the binodal curve.

3.2 The model of the phase boundary.

If cations and anions of an IL had the same affinity to the solvent ($\chi_+ = \chi_-$), because of the symmetry, their concentrations would be equal to each other in all points of the system and the mixture would behave as a binary one. Then the parameter $\tilde{\chi}$ would be the only parameter determining its behavior. Let us consider the general case when the parameters χ_+ and χ_- are different, and, hence, concentrations of the cations and the anions near the phase boundary can be also different. That means appearing of a local electrostatic charge. Density $\rho(\boldsymbol{r})$ of the charge in the point of the mixture described by the vector $\boldsymbol{r}$ is connected with the cations and the anions volume fractions in the point via the relation:

$$\rho(\boldsymbol{r})a^3 = e\left(\varPhi_+(\boldsymbol{r}) - \varPhi_-(\boldsymbol{r})\right) \qquad 3.5$$

where e is the absolute value of an ion's charge, which is supposed to be equal to the elementary charge, and a^3 is the volume of an elementary lattice cell. Let us note that actually in the strict sense $\varPhi_+(\boldsymbol{r})$ and $\varPhi_-(\boldsymbol{r})$ are the volume fractions of elementary lattice cells occupied by the cations and the anions, respectively. But for short they are referred to everywhere in the text of the present dissertation just as the volume fractions of the cations and the anions, respectively.

The energy of the electrostatic field in the system is equal to:

$$E_{el\text{-}st} = \frac{1}{2}\int\limits_V d^3\boldsymbol{r}\rho(\boldsymbol{r})\varphi(\boldsymbol{r}) \qquad 3.6$$

where $\varphi(\boldsymbol{r})$ is the potential of the electrostatic field in the point r and the integral is taken over the whole volume V of the mixture.

The potential $\varphi(\boldsymbol{r})$ and the charge density $\rho(\boldsymbol{r})$ are connected via the Poisson equation:

$$\Delta\varphi(\boldsymbol{r}) = -4\pi\frac{\rho(\boldsymbol{r})}{\varepsilon} \qquad 3.7$$

45

where ε is the dielectric constant of the medium between the charges. This is the dielectric constant the considered mixture would possess if theoretically the charges of its ions disappeared but all other properties of its components stayed the same. In general, this value can't be invariant in space while it must depend on the local mixture composition. But in the first approach we suppose that the value is equal to a constant in all points of the mixture.

There is no electrostatic field far from the phase boundary, i.e. $\varphi'(\pm\infty) = 0$, since the electrostatic charge ρ is localized only at the interface and the system is electroneutral as a whole. Only the gradient of the electrostatic field potential, but not its absolute value is important. Hence it can be assumed for definiteness that $\varphi(-\infty) = 0$. Let us take into account that all the variables describing the system depend only on the coordinate x. After integrating the equation 3.7 and substituting the obtained result in the equation 3.6 one gets the expression describing the contribution $F_{el\text{-}st}$ of electrostatic field to the free energy normalized to the area of the phase boundary:

$$\frac{F_{el\text{-}st}}{kT} = -\frac{2\pi u}{a^2} \int\limits_{-\infty}^{+\infty} dx \int\limits_{-\infty}^{x} dx' \int\limits_{-\infty}^{x'} dx'' \left(\Phi_+(x)-\Phi_-(x)\right)\left(\Phi_+(x'')-\Phi_-(x'')\right) \qquad 3.8$$

where u is the dimensionless parameter equal to the ratio of the adjacent ions electrostatic interaction energy and the thermal energy kT:

$$u = e^2 \big/ kT\,\varepsilon a \qquad 3.9$$

At room temperature, for sodium chloride ions (diameter of a Cl atom is equal to $\sim 2.0*10^{-10}$m and diameter of a Na atom is equal to $\sim 3.6*10^{-10}$m, thus the distance a between their charges when they touch each other is approximately equal to $\sim 2.8*10^{-10}$m) dissolved in water ($\varepsilon \sim 80$) this parameter is of the order of unity. Size of an IL's ions is in average larger than the size of the sodium chloride ions but dielectric constant of an IL is lower than the one of water. So, we assume that the parameter u in the studied system is also of order unity. Let us suppose in this chapter that it is equal to 2.

Let us note that in the expression 3.8 while integration the transformation to dimensionless coordinates has been done. Increase of such a coordinate by one

corresponds to a real spatial shift over one lattice cell size a. In all the following expressions of the present chapter the dimensionless coordinates are used.

Total free energy F_{tot} of the system is composed of the electrostatic field energy F_{el-st}, of the entropic contribution F_{tr-ent} caused by translational motion of the mixture components molecules, and of the term F_{int} appearing due to the molecules Van der Waals interactions:

$$F_{tot} = F_{el-st} + F_{tr-ent} + F_{int} \qquad 3.10$$

The entropic contribution is expressed in the common way:

$$\frac{F_{tr-ent}}{kT} = \frac{1}{a^2} \int_{-\infty}^{+\infty} dx \big(\Phi_+(x) \ln \Phi_+(x) + \Phi_-(x) \ln \Phi_-(x) + \Phi_s(x) \ln \Phi_s(x) \big) \qquad 3.11$$

where $\Phi_s(x)$ denotes the volume fraction of neutral molecules in the having the coordinate x layer parallel to the phase boundary. It is connected with the volume fractions of the cations and the anions via the relation:

$$\Phi_+(x) + \Phi_-(x) + \Phi_s(x) = 1 \qquad 3.12$$

Derivation of the general expression A1.15 describing energy of molecules contact interactions in a spatially nonhomogeneous ternary mixture is presented in the Appendix 1. For the case of the considered in the present chapter one-dimensional system this term can be written as:

$$\frac{F_{int}}{kT} = \frac{1}{a^2} \int_{-\infty}^{\infty} dx \big[\chi_{+-} \Phi(x)_+ \Phi_-(x) + \chi_+ \Phi_+(x) \Phi_S(x) + \chi_- \Phi_-(x) \Phi_S(x) -$$
$$- \frac{1}{6} \big(\chi_{+-} \Phi_+'(x) \Phi_-'(x) + \chi_+ \Phi_+'(x) \Phi_S'(x) + \chi_- \Phi_-'(x) \Phi_S'(x) \big) \big] \qquad 3.13$$

In the expression 3.13 the last three terms are not equal to zero if there exist gradients of the mixture's components concentrations. These are the very terms that provide in the proposed model that the transition zone near the phase boundary has a non-zero thickness. Otherwise the sum of these terms tends to infinity. Like the contribution F_{el-st} to the free energy the contributions F_{int} and F_{tr-ent}, and the total free energy of the system F_{tot} are normalized to the area of the phase boundary.

The equilibrium components concentrations profiles near the phase boundary can be obtained by means of minimization of the F_{tot} functional over the functions $\Phi_+(x)$ and $\Phi_-(x)$. The boundary conditions imposed on these functions are the equalities of the mixture components concentrations far from the boundary to the corresponding concentrations in the two phases that are in equilibrium at the given value of $\tilde{\chi}$. In other words the binodal conditions must be fulfilled (see eq. 3.3):

$$\Phi_+(-\infty) = \Phi_-(-\infty) = \Phi_{-\infty}/2$$

$$\Phi_+(+\infty) = \Phi_-(+\infty) = \Phi_{+\infty}/2 \qquad\qquad 3.14$$

A simplification has been introduced in the calculations related with the search of the functions $\Phi_+(x)$ and $\Phi_-(x)$ corresponding to the minimum of the functional F_{tot}. Namely, the search has been limited. It has been done not among all the continuous functions but only among the trial ones belonging to the collection of exponent step like functions expressed as:

$$\Phi_+(x) = \frac{1}{2}\left(\Phi_{+\infty} + \frac{\Phi_{-\infty} - \Phi_{+\infty}}{1 + \exp(\alpha_+ x)} \right)$$

$$\Phi_-(x) = \frac{1}{2}\left(\Phi_{+\infty} + \frac{\Phi_{-\infty} - \Phi_{+\infty}}{1 + \exp(\alpha_- x)} \right) \qquad\qquad 3.15$$

where α_+ and α_- are the unknown exponent parameters values of which have been determined.

Thus the problem of finding the two optimal functions has been reduced to the problem of finding the optimal values of the two variables α_+ and α_-. All the trial functions belonging to the collection 3.15 fulfill the boundary conditions 3.14 and are obviously similar to the functions $\Phi_+(x)$ and $\Phi_-(x)$ corresponding to the absolute minimum of the functional F_{tot}. Physical meaning of the parameter α_+ (respectively α_-) lies in the fact that its reciprocal is of the same order of magnitude as the thickness of the transition zone in which concentration of the cations (respectively anions) varies from the one constant value $\Phi_{-\infty}/2$ to the other constant value $\Phi_{+\infty}/2$.

Search of the function F_{tot} minimum over the variables α_+ and α_- is equivalent to the system of equations solution:

$$\frac{\partial F_{tot}}{\partial \alpha_+} = 0, \quad \frac{\partial F_{tot}}{\partial \alpha_-} = 0 \qquad\qquad 3.16$$

The system of equations 3.16 has been solved numerically. Let us note that for calculation of the partial derivatives 3.16 one needs to compute numerically the values of the integrals 3.8, 3.11, 3.13 in which the expressions 3.15 are substituted. Analytical treatment allows only a partial simplification of the numerical calculations, for which a lot of computer time is required. Utilization of any numerical algorithm for solution of the system 3.16 requires a manifold calculation of the partial derivatives at different values of α_+ and α_-. Moreover in the present study the system of equations 3.16 must be solved many times at different values of the Flory-Huggins parameters characterizing the system.

For this reason, the calculation process has been speeded up in the following way. At first all the possible integrals appearing while the calculation of the derivatives 3.16 have been computed for the given set of possible different values of the variables α_+, α_-, and $\Phi_{+\infty}$. In other words, integral tables have been created. As a result, the possibility has appeared to obtain fast the required values of the derivatives 3.16 for any set of the variables α_+, α_-, and $\Phi_{+\infty}$ just by means of interpolation of the taken from these tables data that correspond to the closest values of these variables.

As soon as the equilibrium values of α_+ and α_- are known the structure of the phase boundary is determined and its surface tension σ can be calculated in the following way. Let us imagine that there are two separate volumes of homogeneous mixture in which volume fractions of the IL are equal to $\Phi_{+\infty}$ and $\Phi_{-\infty}$. Let us imagine that the volumes are brought into contact. Then, by definition, the resulting increase of their total free energy normalized to the area of the emerged phase boundary surface is exactly equal to the surface tension of the boundary. That is:

$$\sigma = F_{tot} - F_0 \qquad\qquad 3.17$$

where

$$\frac{F_0}{kT} = \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad 3.18$$

$$= \frac{1}{a^2} \int_{-\infty}^{0} dx \left\{ \Phi_{-\infty} \ln \frac{\Phi_{-\infty}}{2} + (1 - \Phi_{-\infty}) \ln(1 - \Phi_{-\infty}) + \chi_{+-} \frac{\Phi_{-\infty}^2}{4} + \chi \Phi_{-\infty} (1 - \Phi_{-\infty}) \right\} +$$

$$+ \frac{1}{a^2} \int_{0}^{+\infty} dx \left\{ \Phi_{+\infty} \ln \frac{\Phi_{+\infty}}{2} + (1 - \Phi_{+\infty}) \ln(1 - \Phi_{+\infty}) + \chi_{+-} \frac{\Phi_{+\infty}^2}{4} + \chi \Phi_{+\infty} (1 - \Phi_{+\infty}) \right\}$$

It is worthy to be noted that as a matter of fact the values F_{tot} and F_0 are not defined, because they depend on the thickness of the mixture layers at the both sides from the phase boundary, which are assumed in the model to be infinite. But in the considered calculations only the difference of the two values and their derivatives are used. As to the difference and the derivatives, they are well defined, since they depend on the properties of the phase boundary only.

3.3 The obtained results.

Let us assume for definiteness, that $\Phi_{-\infty} > \Phi_{+\infty}$, and the cations are less compatible with the neutral molecules than the anions, i.e. $\chi_+ > \chi_-$. Then the thickness of the near-boundary transition layer in which the concentration of the cations varies, is less than the thickness of the corresponding layer of anions, i.e. $1/\alpha_+ < 1/\alpha_-$.

Let us introduce the parameter $\Delta\chi$:

$$\Delta\chi = (\chi_+ - \chi_-)/2 \qquad\qquad\qquad\qquad\qquad 3.19$$

This parameter characterizes difference in the affinities of the anions and of the cations of the IL to the molecules of the nIL. To characterize the system under investigation it is more convenient to use the set of parameters ($\tilde{\chi}$, $\Delta\chi$, χ_{+-}) than the equivalent to it set (χ_+, χ_-, χ_{+-}). Our calculations have shown that at fixed values of the parameters $\tilde{\chi}$ and $\Delta\chi$ variation of the parameter χ_{+-} doesn't influence significantly the structure of the phase boundary. (Different plots illustrating this fact are not of interest and for this reason are not presented here.)

That's why it is supposed in the present chapter for definiteness that the value of χ_{+-} is equal to zero.

In the figure 6 a typical ions distribution near the phase boundary is presented. It corresponds to the set of parameters ($\tilde{\chi} = 3$, $\Delta\chi = 5$), at which, as our calculations have shown, the values of the exponent parameters α_+ and α_- are equal to 2.6 and 2, respectively. The curves *a)* and *b)* represent the dependencies of the volume fractions of the cations and the anions, respectively, on the coordinate x perpendicular to the phase boundary. The volume fractions are normalized to their maximal value $\Phi_{-\infty}/2$. The curve *c)* represents the dependence on x of the local charge density $\tilde{\rho}$, that is also normalized to its maximal value.
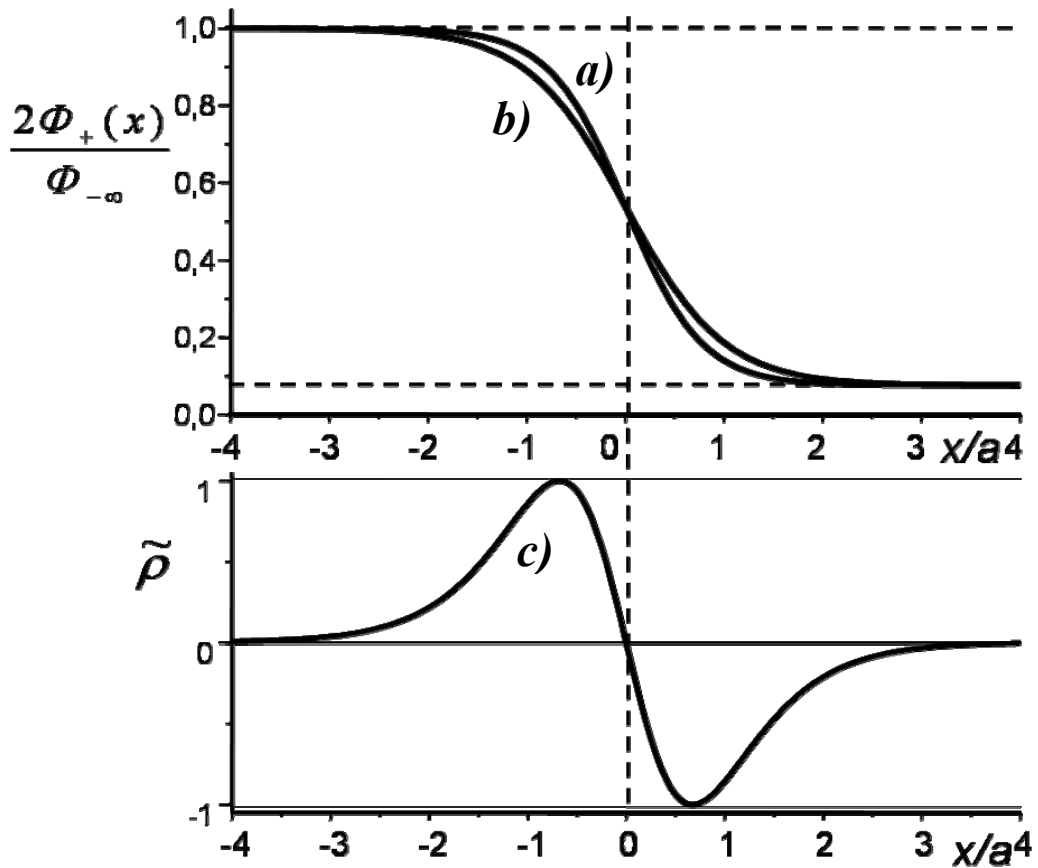
Figure 6. Dependence of the volume fractions of the cations (*a*) and the anions (*b*) of an IL, and of the electrostatic charge density (*c*), normalized to their maximal values, on the coordinate x, perpendicular to the phase boundary. $\tilde{\chi} = 3$, $\Delta\chi = 5$, $\chi_{+-} = 0$, $u = 2$.

It can be seen that if the affinities of the cations and the anions to the neutral molecules are different ($\Delta\chi \neq 0$) there appear two layers near the phase boundary. One of them is charged positively and the other one is charged negatively. As a result, an electrostatic field appears near the phase boundary. The figure 7 represents the dependence of this double layer electrostatic energy on the parameter $\Delta\chi$. The energy is normalized to the thermal energy kT and to the total number of elementary cells composing one layer parallel to the phase boundary. Two different curves correspond to different values of the parameter $\tilde{\chi}$: $\tilde{\chi} = 4$ a), $\tilde{\chi} = 2.5$ b).

One can see on the plot that the energy of electrostatic field increases with the growth of the difference in affinities of the IL's cations and the IL's anions to the neutral molecules and also with the growth of incompatibility of the IL as a whole to the nonionic solvent. Let us note that possibility of such a double
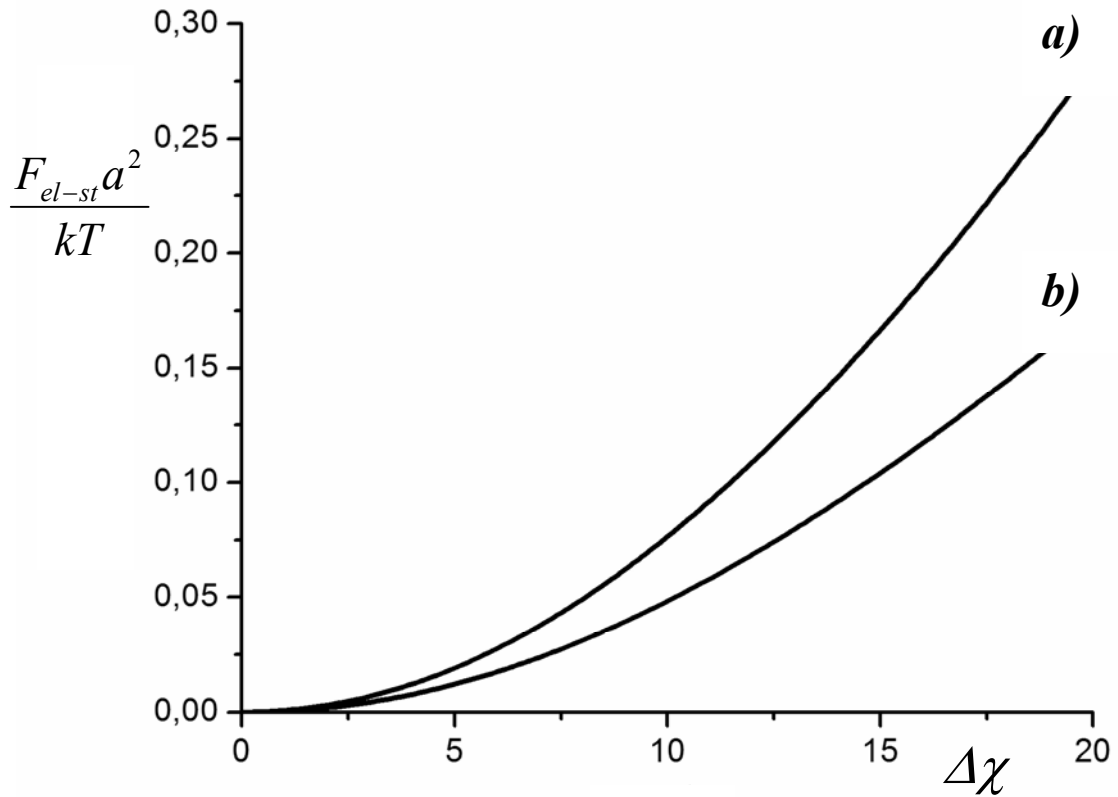

Figure 7. Dependence of the electrostatic field free energy $F_{el\text{-}st}\,a^2/kT$ on the value of the parameter $\Delta\chi$. The energy is normalized to the thermal motion energy and to the total number of elementary cells composing one layer parallel to the phase boundary. $\tilde{\chi} = 4$ (a), $\tilde{\chi} = 2.5$ (b), $\chi_{+-} = 0$, $u = 2$.

electrostatic layer appearing has been proved experimentally in the work [69].

Main results of our numerical calculations are presented in the figures 8-12. Curves *a)* and *b)* in all the figures represent dependencies of the exponent parameters α_+ and α_-, respectively, on the difference in affinities $\Delta\chi$ of the IL's cations and the IL's anions to the neutral molecules. The curves *c)* represent dependence of the dimensionless phase boundary surface tension on the same variable. Dimensionless surface tension of the phase boundary is its energy normalized to kT and to the total number of elementary cells composing one layer parallel to the boundary. The only difference between the figures 8-12 is that they correspond to different values of the parameter $\tilde{\chi}$.

The thickness of the zone where both concentrations of the cations and of the anions of the IL vary from their one constant value to their other constant
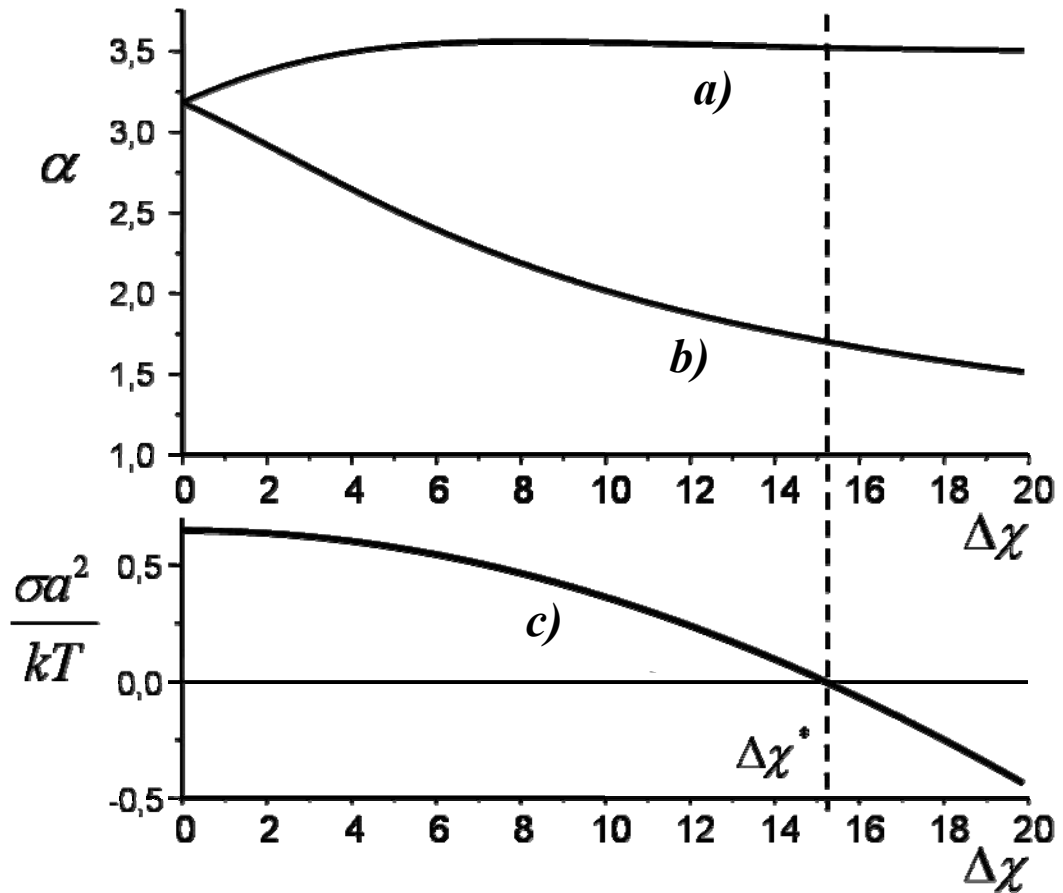

Figure 8. Dependence of the exponent parameters α_+ (*a*) and α_- (*b*), and of the dimensionless surface tension $\sigma a^2/kT$ of the phase boundary (*c*) on the value of the parameter $\Delta\chi$ at $\tilde{\chi} = 4$, $\chi_{+-} = 0$, $u = 2$.

value can be treated as the thickness of the phase boundary. That is, the thickness of the phase boundary is of the same order of magnitude as the maximal of the two values $(1/\alpha_+, 1/\alpha_-)$. Since it is assumed that $\chi_+ > \chi_-$ the thickness is of the same order of magnitude as $1/\alpha_-$.

The following can be seen in the figures 8-12. The higher is the value of $\Delta\chi$, the higher is the difference of the values α_+ and α_- reciprocal to the sizes of the concentration transition zones of the cations and the anions. Since concentrations of the IL in the bulk of the adjacent phases depend on the value of the parameter $\tilde{\chi}$ (see figure 5) it is reasonable that the value of this parameter influences also the structure of the interface between the phases.

It can be seen in the figures 8-12 that at $\Delta\chi = 0$ the concentrations profiles of the cations and the anions coincide. This means that there is no double electrostatic layer and the system behaves as a binary one, as it has been already
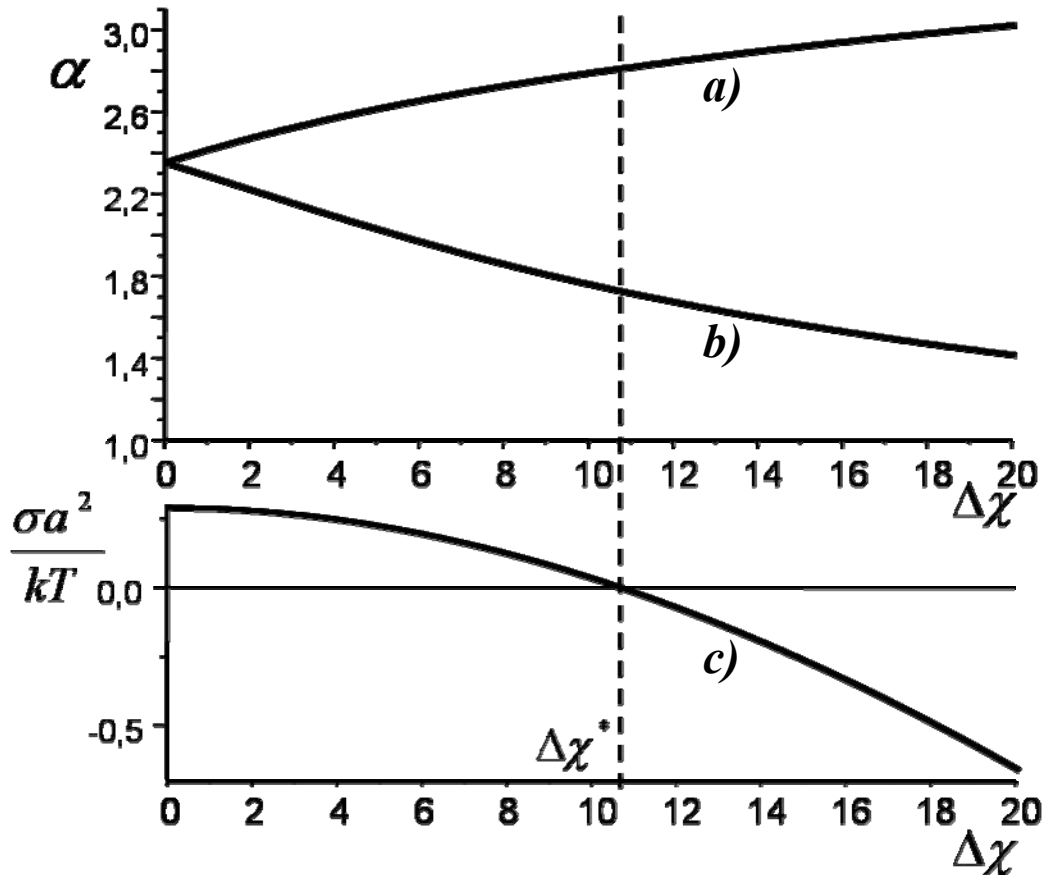

Figure 9. Dependence of the exponent parameters α_+ (*a*) and α_- (*b*), and of the dimensionless surface tension $\sigma a^2/kT$ of the phase boundary (*c*) on the value of the parameter $\Delta\chi$ at $\tilde{\chi} = 3$, $\chi_{+-} = 0$, $u = 2$.

mentioned. In this case the thickness of the phase boundary grows with the decrease of $\tilde{\chi}$. In other words, the closer are the compositions of the two phases the more stretched is the transition zone between them. The reason is that the decrease of the parameter $\tilde{\chi}$ means the increase of the IL affinity as a whole to the nonionic solvent. This in its turn means, that a deeper interpenetration of the two liquids becomes more favorable. When the parameter $\tilde{\chi}$ tends to the critical value of 2, at which any difference between the two phases disappears and macrophase separation becomes impossible, the thickness of the phase boundary tends to infinity.

As the value of the parameter $\Delta\chi$ grows the influence of the parameter $\tilde{\chi}$ on the thickness of the phase boundary becomes less pronounced. If the value of $\tilde{\chi}$ is significantly higher than the critical value of 2 (see figure 8), i.e. the IL and
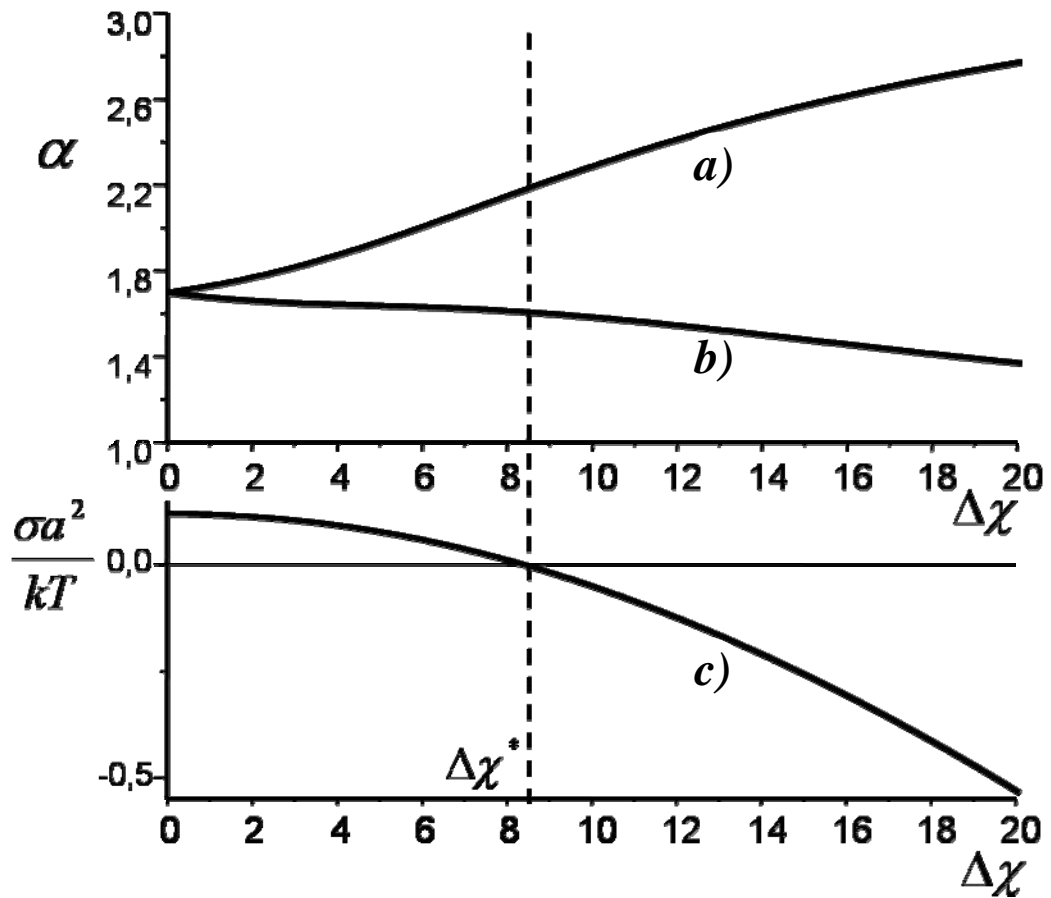

Figure 10. Dependence of the exponent parameters α_+ (*a*) and α_- (*b*), and of the dimensionless surface tension $\sigma a^2/kT$ of the phase boundary (*c*) on the value of the parameter $\Delta\chi$ at $\tilde{\chi} = 2.5$, $\chi_{+-} = 0$, $u = 2$.

the nIL are poorly mixable, then the thickness of the phase boundary grows with the increase of $\Delta\chi$. Vice versa, if the value of $\tilde{\chi}$ is close to the critical value of 2 (see figure 12), i.e. the IL and the nIL are almost completely mixable, then the thickness of the phase boundary decreases with the increase of $\Delta\chi$.

If one analyses the curves c) of the figures 8-12 one can notice that the phase boundary surface tension is always positive if $\Delta\chi$ is equal to zero and as the value of $\Delta\chi$ increases the surface tension decreases monotonically. One can conclude that the separation of the cations and the anions near the phase boundary is the very reason of the surface tension decrease.

Moreover, if the difference in affinities of the cations and the anions to the neutral molecules exceeds a certain threshold level (i.e. if the value of the parameter $\Delta\chi$ exceeds the certain threshold value $\Delta\chi^*$) then the surface tension of the phase boundary becomes negative. The latter means that the larger is the area
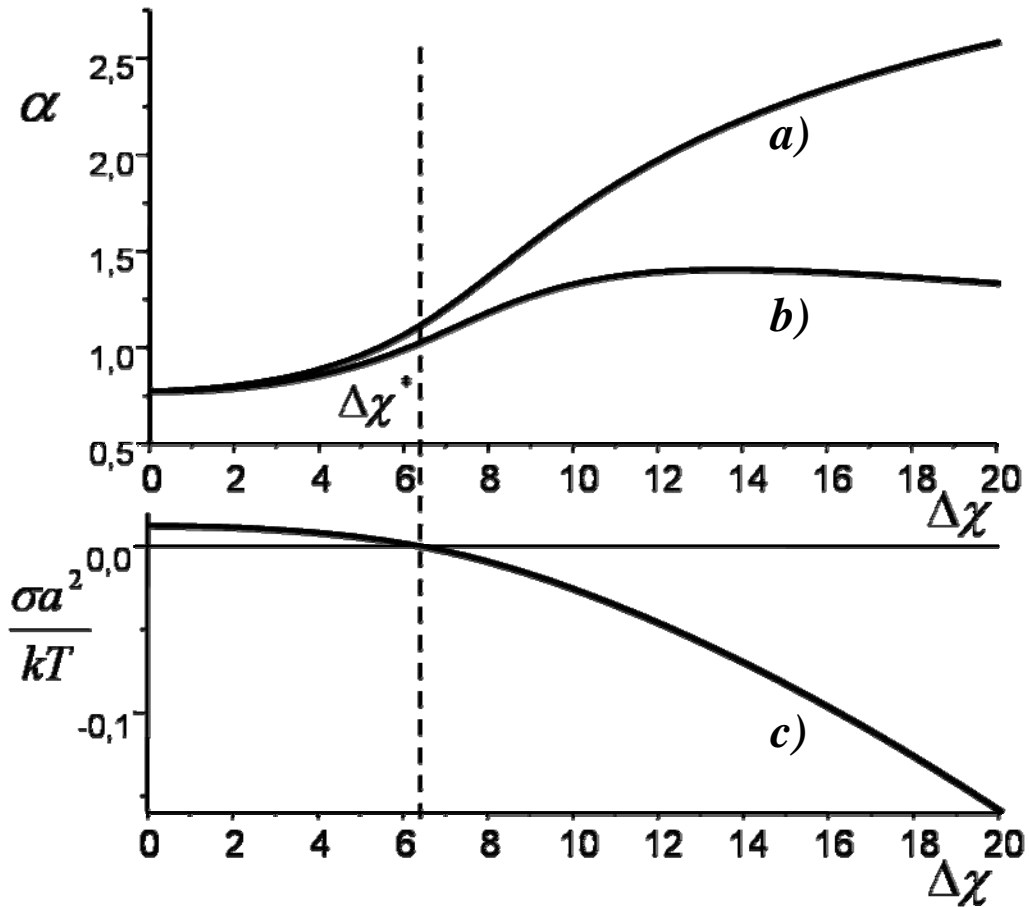

Figure 11. Dependence of the exponent parameters α_+ (a) and α_- (b), and of the dimensionless surface tension $\sigma a^2/kT$ of the phase boundary (c) on the value of the parameter $\Delta\chi$ at $\tilde{\chi}=2.1$, $\chi_{+-}=0$, $u=2$.

of the boundary separating the two phases, the lower is the free energy of the system. Hence, the area of the phase boundary must unrestrictedly grow and, thus, existence of two individual macrophases is, as a matter of fact, in this case impossible. It can be seen in the figures 8-12 that the critical value $\Delta\chi^*$ grows with the increase of $\tilde{\chi}$.

Thus, if in a IL/nIL mixture the average volume fraction Φ of IL and the characterized by the parameter $\tilde{\chi}$ affinity of the components to each other correspond to the point on the phase diagram in coordinates (Φ, $\tilde{\chi}$) (see figure 5) that is located over the binodal curve, then the mixture on the one hand can't be homogeneous. But on the other hand, if in addition $\Delta\chi > \Delta\chi^*$, then a macrophase separation of the mixture is also impossible. Hence, a microheterogeneous structure must be formed in the system.
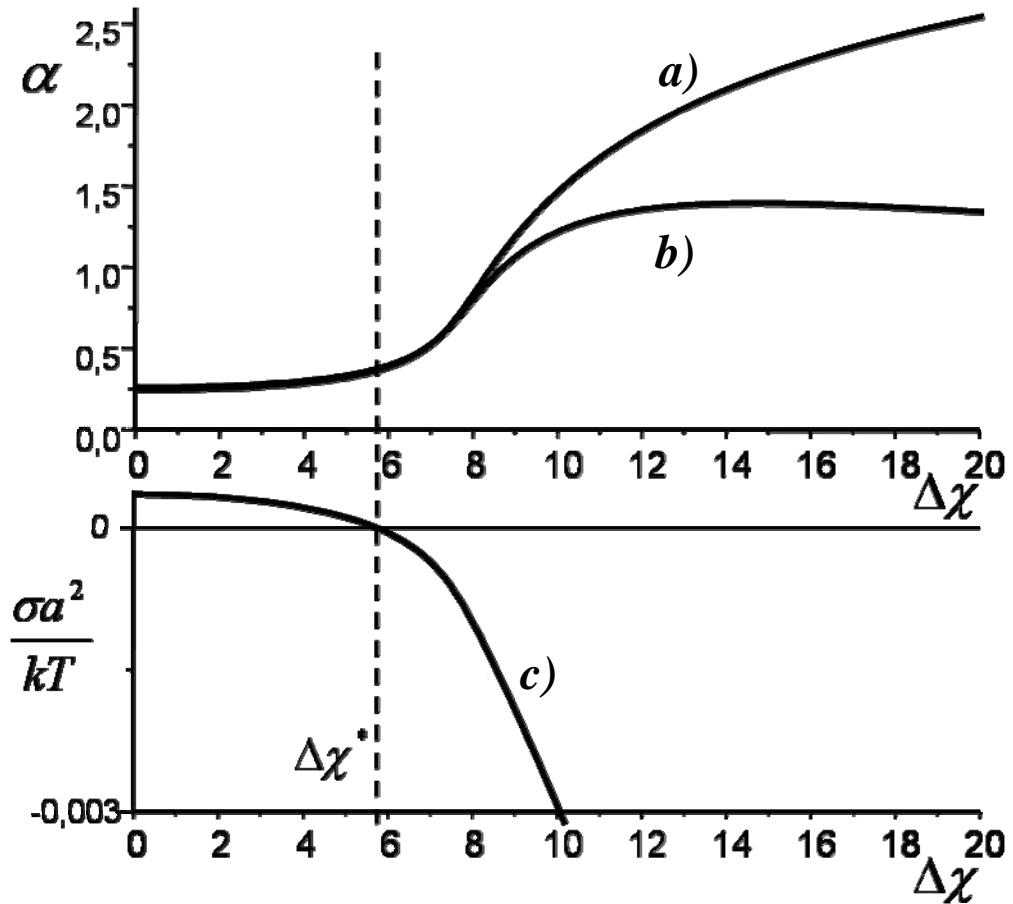

Figure 12. Dependence of the exponent parameters α_+ (*a*) and α_- (*b*), and of the dimensionless surface tension $\sigma a^2/kT$ of the phase boundary (*c*) on the value of the parameter $\Delta\chi$ at $\tilde{\chi} = 2.01$, $\chi_{+-} = 0$, $u = 2$.

This is in agreement with the results of the computer simulation works [70] and [71] in which microphase separation in a pure IL and in a IL/nIL mixture, respectively, has been also predicted. Besides possibility of a microheterogeneous clathrate structure origination in IL/benzene mixtures has been proved experimentally [72,73].

In the previous chapter it has been demonstrated that the solvent power of an IL grows with the increase of the incompatibility of the IL's cations and the IL's anions. This means that if the parameter χ is fixed a mixture of an IL and a nIL turns into a homogeneous one if the parameter χ_{+-} exceeds a certain threshold value. In the present chapter this statement is extended. Namely, if existence of a homogeneous IL/nIL mixture is impossible, while the value of $\widetilde{\chi}$ doesn't allow that, then there still remains a possibility that the two substances can be intermixed by means of forming a microheterogeneous structure. The latter is possible if the difference in the IL's cations and anions affinities to the molecules of the nonionic liquid is high enough.

In the figure 13 the phase diagram of a mixture IL/nIL in the coordinates $(\widetilde{\chi}, \Delta\chi)$ is presented. There are three domains on the phase diagram that correspond to the three possible states of the system: homogeneous mixture, microheterogeneous mixture, and macrophase separation. The mixture is homogeneous if the value of the parameter $\widetilde{\chi}$ is less than the threshold value $\widetilde{\chi}^{*}$ which is determined from the binodal condition (see figure 5 and the equation 3.3). The phase diagram presented on the figure 13 corresponds to a mixture in which the volume fraction Φ of IL is equal to 0.5. Hence in this case $\widetilde{\chi}^{*} = 2$. As to the curve which is the boundary between the macrophase separation domain and the microheterogeneous state domain, it is obtained from the condition of equality to zero of the phase boundary surface tension. Actually, this curve is the dependence of $\Delta\chi^{*}$ on $\widetilde{\chi}$ taken from the set of the figures 8-12.

At a given value of $\widetilde{\chi}$ macrophase separated state and microheterogeneous state of the system are possible only if the average volume fraction Φ of IL in the
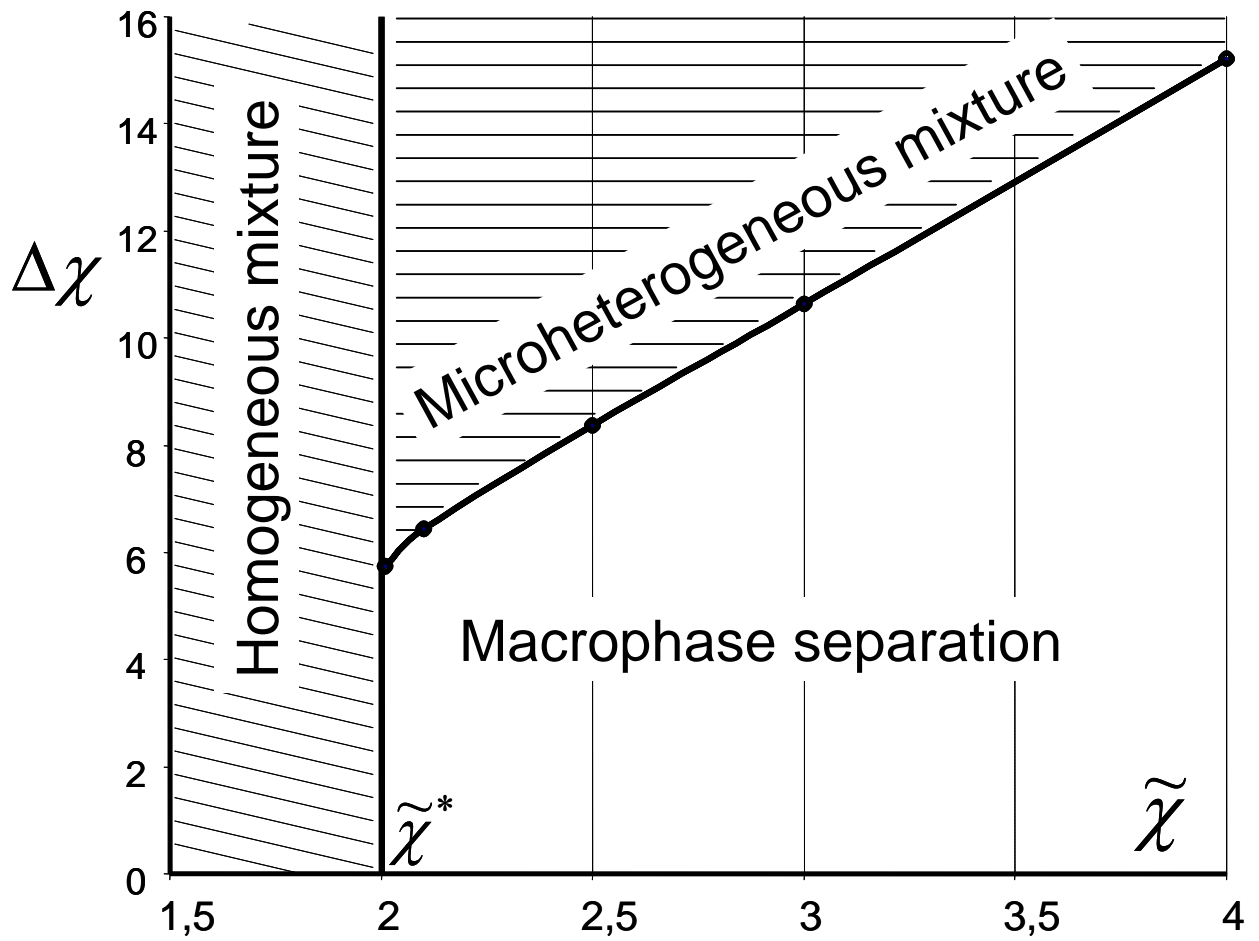
Figure 13. Phase diagram of the IL/nIL mixture in the coordinates $(\widetilde{\chi}, \Delta\chi)$, at $\Phi = 0.5$, $\chi_{+-} = 0$, $u = 2$.

mixture is such that $\widetilde{\chi} > \widetilde{\chi}^*$. But the location on the phase diagram (figure 13) of the boundary between the macrophase separated state and the microheterogeneous state doesn't depend on Φ.

How does the mentioned microheterogeneous state of the mixture IL/nIL look like? One can suppose that if the concentration of IL is not very high, then clusters can be formed in the system, like it occurs in polymer systems [74,75]. In the considered case the clusters consist of ions. They have a certain optimal radius and between the clusters there is a homogeneous solution in which volume fraction of the IL is much lower than its average volume fraction in the system.

The microheterogeneous structure of the mixture is schematically presented in the figure 14. The gray and the unpainted circles represent the

cations and the anions of the IL, respectively. As to the neutral molecules of the nIL, they occupy the rest of the mixture volume and are not depicted.

As a whole, the clusters are electroneutral, but not homogeneous. The IL's anions, which have a higher affinity to the nIL, are located closer to the surface of the cluster, while the cations are in average closer to its center. However the cations and the anions can't disperse, since they are held by the localized in the clusters electrostatic field. The size of the clusters is determined by the balance of the long-range electrostatic interactions and the short-range contact interactions [74,75]. Let us mention here that the formation of such IL clusters (micelles) in a nIL (water) has been recently observed in experiment [76]. At higher average concentrations of IL in the mixture a more intricate microstructure with a spatially nonuniform distribution of the IL's ions is to be formed instead of separate IL clusters.
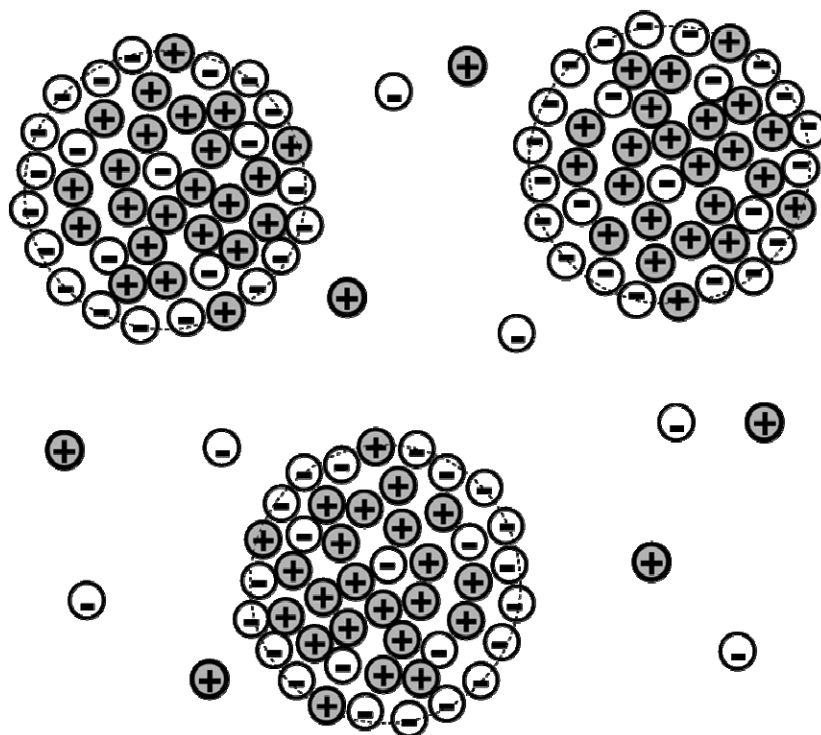

Figure 14. Schematic illustration of the ion cluster that can be formed in a IL/nIL mixture. The cations and the anions are represented by gray and unpainted circles, correspondingly. The neutral molecules occupying the rest of the mixture volume are not depicted.

The microheterogeneous IL/nIL mixture can be useful in application to heterogeneous catalysis. Let us suppose that a catalyst is immobilized in an IL which serves as one of the two phases of the system, and the reagent is dissolved in the other phase (a nIL). The reaction in which they are involved takes place as the reagent diffuses through the phase boundary into the IL. The reaction rate obviously increases with the growth of the two phases contact surface [77,78]. Hence, the reaction rate is to be maximal if the IL and the nIL form a microheterogeneous mixture. Besides, if in the given mixture the value of the parameter $\Delta\chi$ is close to the critical value $\Delta\chi^*$ the reaction rate can be effectively controlled by means of varying the system's temperature and thus making the system transfer from the macrophase separated state to the microheterogeneous state and back.

Let us briefly summarize the chapter 3. The phase boundary between an IL and a nIL has been investigated. It has been found out that a double electrostatic layer is formed at the boundary and the electrostatic energy of the layer is the higher the higher is the difference in the affinities of the IL's cations and the IL's anions to the to the neutral molecules.

If the IL as a whole is poorly mixable with the nIL then the thickness of the phase boundary increases with the growth of the difference in the affinities of the IL's cations and the IL's anions to the neutral molecules. Vice versa, if the IL and the nIL are almost absolutely mixable, the thickness of the phase boundary decreases.

The surface tension of the phase boundary decreases with the increase of the compatibility of the nIL and the IL as a whole. The surface tension decreases also with the growth of the difference in the affinities of the IL's cations and the IL's anions to the neutral molecules.

If the difference in the affinities of the IL's cations and the IL's anions to the neutral molecules is higher than a certain threshold value then formation of a microheterogeneous structure is possible in the IL/nIL mixture. This threshold value is the higher the lower is the compatibility of the IL and the nIL.

4. Microphase separation in a mixture of an ionic liquid and a nonionic liquid.

The present chapter [20] is devoted to the started in the previous chapter investigation of the possibility of a microheterogeneous IL/nIL mixture existence. As in the previous two chapters the study is focused on the influence of the contact interactions of the mixture components on the behavior of the mixture. The mixture is treated again as a ternary one and again the lattice model is used with the same main assumptions and the same notation of the parameters characterizing the components contact interactions (see figure 3 and the expressions 2.6, 3.4 and 3.19). This time the subject of the investigation is the stability of the system in its spatially homogeneous state towards microphase separation. As the instrument of the investigation the so-called random phase approximation technique is utilized. The same technique is used for theoretical investigation of microphase separation in polymer systems [79-81].

Let us suppose that a small perturbation of the homogeneous IL/nIL mixture has spontaneously appeared and, as a result of it, the volume fractions of the IL's cations and anions in an arbitrary point r of the system have become equal to:

$$\Phi_+(r) = \Phi/2 + \delta\Phi_+(r)$$
$$\Phi_-(r) = \Phi/2 + \delta\Phi_-(r)$$

4.1

where $\delta\Phi_+(r)$ and $\delta\Phi_-(r)$ are the small fluctuations of volume fractions of the cations and the anions, respectively, and $\Phi/2$ is the average value of the cations and the anions volume fractions. As to the fluctuation $\delta\Phi_S(r)$ of the neutral molecules volume fraction, it follows from the assumption of the mixture incompressibility that it is connected with the fluctuations of the cations and the anions volume fractions via the relation:

$$\delta\Phi_S(r) + \delta\Phi_+(r) + \delta\Phi_-(r) = 0$$

4.2

Besides, since when the fluctuations appear in the mixture, total amounts of the components in the mixture are not changed, the following equations must be fulfilled:

$$\int_V \delta\Phi_S(r)d^3r = \int_V \delta\Phi_+(r)d^3r = \int_V \delta\Phi_-(r)d^3r = 0 \qquad\qquad 4.3$$

where the integration is carried out over the whole volume V of the mixture. It is also supposed that the functions $\delta\Phi_+(r)$ and $\delta\Phi_-(r)$ are continuous and their gradients are not large.

We investigate if the free energy of the system decreases when the aforementioned perturbation appears in it. Let us suppose that the appeared in the system fluctuation of the cations (the anions) volume fraction is a harmonic one described by the following expression:

$$\delta\Phi_{+(-)}(r) = A_{+(-)}\cos(qr) \qquad\qquad 4.4$$

where $A_{+(-)}$ is the amplitude of the cations (the anions) volume fraction fluctuation and q is the wave vector. If one minimizes the free energy of the system over all possible fluctuations of the anions (or the cations, respectively) volume fraction, one obtains that the minimal additive δF to the system's free energy, that corresponds to the given fluctuation of the cations (the anions) volume fraction is equal to:

$$\frac{\delta F a^3}{kTV} = G(q)\frac{A^2_{+(-)}}{2} \qquad\qquad 4.5$$

where the value G is expressed as:

$$G = -\chi - \Delta\chi + \frac{1}{\Phi} + \frac{1}{2(1-\Phi)} + \frac{\tilde{q}^2}{6}(\chi + \Delta\chi) + \frac{2\pi u}{\tilde{q}^2} -$$

$$-\frac{1}{4}\frac{\left(\chi_{+-} - 2\chi + \dfrac{1}{(1-\Phi)} + \dfrac{\tilde{q}^2}{6}(-\chi_{+-} + 2\chi) - \dfrac{4\pi u}{\tilde{q}^2}\right)^2}{-\chi + \Delta\chi + \dfrac{1}{\Phi} + \dfrac{1}{2(1-\Phi)} + \dfrac{\tilde{q}^2}{6}(\chi - \Delta\chi) + \dfrac{2\pi u}{\tilde{q}^2}} \qquad\qquad 4.6$$

where $\widetilde{q} = qa$ is the dimensionless wave vector. The theoretical justification of why the additive to the free energy is expressed by the equations 4.5 and 4.6 is presented in the appendix 2 of the present dissertation. Let us shortly identify the value δF as the free energy of the fluctuation to which it corresponds.

Let us note that the value G depends only on the modulus $\widetilde{q}$ of the wave vector $\widetilde{q}$. If G is positive at all values of $\widetilde{q}$ then the homogeneous state of the system is stable because the corresponding to it free energy is less than in any of the perturbed states. This is due to the fact that any function $\delta\Phi_{+(-)}(r)$ can be expressed as a linear combination of harmonic components of the type described by the equation 4.4. As to the free energy of the fluctuation $\delta\Phi_{+(-)}(r)$, it is exactly equal to the sum of the harmonic components free energies (see the appendix 2 and the formulas A2.12, A2.14).

But if the value G is negative at a certain nonzero value of $\widetilde{q}$ which is less than unity, then the spatially homogeneous state of the system is not stable, since there exists a microheterogeneous structure with the spatial period $a/\widetilde{q}$, which possesses a lower free energy, whatever small is the amplitude of the concentration fluctuation in the structure. (The values of $\widetilde{q}$ that are larger than unity are excluded because they correspond to unreal microstructures having spatial periods smaller than the diameter a of a molecule.)

In other words, on the phase diagram, the boundary of the zone of the homogeneous mixture stability towards microphase separation (the spinodal curve of microphase separation) is determined by the conditions of equality to zero of the function $G(\widetilde{q})$ minimum. That is:

$$G(\widetilde{q}^{*}) = 0, \qquad \partial G/\partial \widetilde{q}^{*} = 0 \qquad\qquad 4.7$$

where $\widetilde{q}^{*}$ is the value of the wave vector modulus $\widetilde{q}$ at which the function $G(\widetilde{q})$ reaches its minimal value.

If the value G first reaches zero at $\tilde{q}=0$, then in the system a microphase separation with an infinitely large size of heterogeneities is to start. In other words, it means that a macrophase separation is to take place in the system.

The system of equations 4.7 can be solved numerically, and at first the problem has been solved by us in this wise. However, it has been noticed later that the same results with only minor deviations can be obtained also analytically with the help of some approximations. Namely, let us expand the value G into series of the value $\tilde{q}$ powers and leave only the three terms of the highest order:

$$G \approx G_0 + B\tilde{q}^2 + C\tilde{q}^4 \qquad\qquad 4.8$$

where:

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

$$B = \frac{2}{3}\tilde{\chi} - \frac{\left(G_0 + 2\Delta\chi\right)^2}{8\pi u}, \qquad\qquad 4.9$$

$$C = \left(\frac{1}{2\Phi} + \frac{G_0 - \chi_{+-}}{4} + \Delta\chi\right)\frac{\left(G_0 + 2\Delta\chi\right)^2}{16\pi^2 u^2} - \frac{\left(G_0 + 2\Delta\chi\right)\ \left(2\tilde{\chi} - \Delta\chi\right)}{12\pi u}$$

As our numerical estimates have shown, the expansion 4.9 is a good approximation of the value G up to the value of $\tilde{q}$ reaching 0.2. Higher values of $\tilde{q}$ are anyway of no interest, because they correspond to microstructures having a very short spatial period, for which the utilized here model is not well applicable. Namely, first, using of the expression A2.9 comprising gradient terms implies that only smooth concentration fluctuations are considered. Second, it is assumed in the utilized model that the sizes of all the mixture components molecules are the same. But if the microheterogeneous structure of a mixture has a very small period, the difference in the components molecules sizes is obviously important and must be taken into account if one needs to describe the properties of the structure.

So, below, only small values of $\tilde{q}$ are considered, and the expression 4.8 is used for representing of the value G. Let us build the spinodal of the mixture IL/nIL. As in the previous chapter, for definiteness we assume that $\chi_{+-}= 0$. If the value B is positive, then the expression 4.8 can turn into zero only at $\tilde{q} = 0$, if the value of G_0 is equal to zero. As it has been already mentioned, this means that only macrophase separation can take place in the system, and, obviously, the equality of G_0 to zero is nothing else than the mixture IL/nIL macrophase separation spinodal condition (see eq. 2.7).

If $B<0$, the value G has a minimum at a positive value of the wave vector modulus equal to:

$$\tilde{q}^* = \left(-\frac{B}{2C} \right)^{1/2}$$ 4.10

In this case, as it follows from the equations 4.7, microphase separation becomes possible in the system if:

$$G_0 - \frac{B^2}{4C} = 0$$ 4.11

It follows from the equations 4.10 and 4.11 that:

$$\left(\tilde{q}^* \right)^2 = \sqrt{\frac{G_0}{C}}$$ 4.12

Since in the considered space of the parameters characterizing the system, the value C is of order unity (as it is known from our numerical calculations), and only small values of $\tilde{q}$ are considered, the value of G_0 is very small on the considered spinodal (even if the value $\tilde{q}^*$ doesn't exceed 0.3 it follows from the expression 4.12 that then the value of G_0 is less than 0.01). That's why after substituting the expressions 4.9 representing the values B and C into the equation 4.11 an expansion into series of the G_0 powers can be done and terms only of the highest order can be left. Moreover, since the value of G_0 is very small on the considered spinodal, it can be

roughly assumed that the equality $\widetilde{\chi} = 1/2\Phi(1-\Phi)$ is valid (see the equation 4.9). As a result, the following approximate expression describing the microphase separation spinodal can be obtained:

$$\Delta\chi = \sqrt{\frac{2\pi u}{3\Phi(1-\Phi)}} + \sqrt{6\pi Cu\Phi(1-\Phi)G_0} \qquad 4.13$$

One can see that if $\Delta\chi < \Delta\chi_{min} = (8\pi u/3)^{1/2}$ then the equation 4.13 can't be fulfilled, i.e. the microphase separation is not possible. This follows from the fact that the minimal value of the second term in 4.13 is equal to zero (if $G_0 = 0$) and the minimal value of the first term is attained at $\Phi = 0.5$. If the value of $\Delta\chi$ is fixed, the stronger Φ differs from 0.5 the less is the value of G_0. When the value of G_0 turns into zero the microphase separation spinodal coincides with the macrophase separation spinodal. As it follows from the equation 4.13, this is fulfilled if:

$$\widetilde{\chi} = \frac{3\Delta\chi^2}{4\pi u} \qquad 4.14$$

In the points where spinodal curves of microphase and macrophase separation coincide ($B = 0$, $G_0 = 0$), the so-called Lifshitz points [82], the value of B changes its sign (see the equation 4.9). Hence, the Lifshitz points determine the boundaries of the microphase separation domain.

In the figure 15 the spinodal curves of the mixture IL/nIL are presented in the coordinates (Φ, $\widetilde{\chi}$) for two different values of the parameter $\Delta\chi$: $\Delta\chi = 3$ (a), $\Delta\chi = 2.7$ (b). The value of $4\pi u$ has been taken to be equal to 10. For this value of u the value of $\Delta\chi_{min}$ is approximately equal to 2.58. P_1, P_2 and M_1, M_2 are the Lifshitz points of the curves (a) and (b), respectively. The Lifshitz points are located symmetrically with respect to the value of $\Phi = 0.5$, because if $G_0 = 0$, the expression 4.13 is symmetrical with respect to interchang of Φ and $1 - \Phi$. One can see that the larger is the value of $\Delta\chi$, the lower is the part of the spinodal curve that is located between the Lifshitz points and corresponds to the microphase separation. As to the
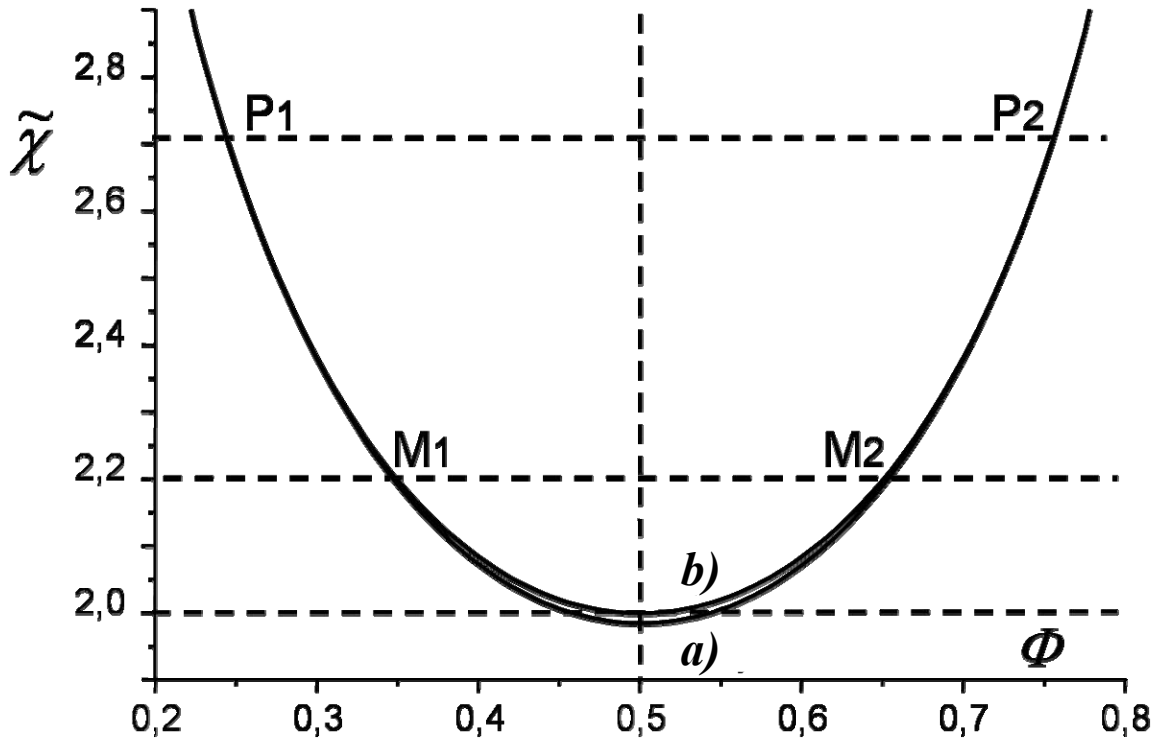
Figure 15. Spinodal of the IL/nIL mixture at $\Delta\chi = 3$ (*a*), $\Delta\chi = 2.7$ (*b*), $\chi_{+-} = 0$, $4\pi u = 10$. P_1, P_2 and M_1, M_2 are the Lifshitz points for the cases (*a*) and (*b*), respectively.

parts of the spinodal curve that are located on the outside of the Lifshitz points, they coincide with the spinodal curve of the mixture's macrophase separation. The larger is $\Delta\chi$ the larger is the value $\tilde{\chi}$ corresponding to the Lifshitz points, and the broader is the microphase separation domain on the phase diagram.

The physical meaning of the phase diagram presented on the figure 15 is the following. If a point with the coordinates $(\Phi, \tilde{\chi})$ is located below the spinodal curve, then the mixture to which the point corresponds is to be homogeneous. If now the parameters describing the mixture are changed in such a way that the point overpasses the spinodal curve, then a phase separation is to take place in the mixture. Herein two cases are possible. Namely, if the spinodal curve is overpassed in its part located between the Lifshitz points then a m*i*crophase separation is to take place in

the system. But if the curve is overpassed in any of the two parts lying on the outside of the Lifshitz points, then a *m**a*crophase separation is to take place in the system.

Thus, if the values of the parameters $\Delta\chi$ and u are fixed the microphase separation of the IL/nIL mixture becomes possible if the value of the parameter $\widetilde{\chi}$, characterizing interaction of the mixture's two components, is less than the threshold value determined by the expression 4.14, or, in other words, if the ordinate of the Lifshitz points on the presented on the figure 15 phase diagram is larger than $\widetilde{\chi}$.

In the figure 16 the phase diagram of the system in the coordinates ($\widetilde{\chi}$, $\Delta\chi$) is presented, which illustrates the stated above. The value of the parameter u is taken to be equal to 2 as in the case presented in the previous chapter on the phase diagram in
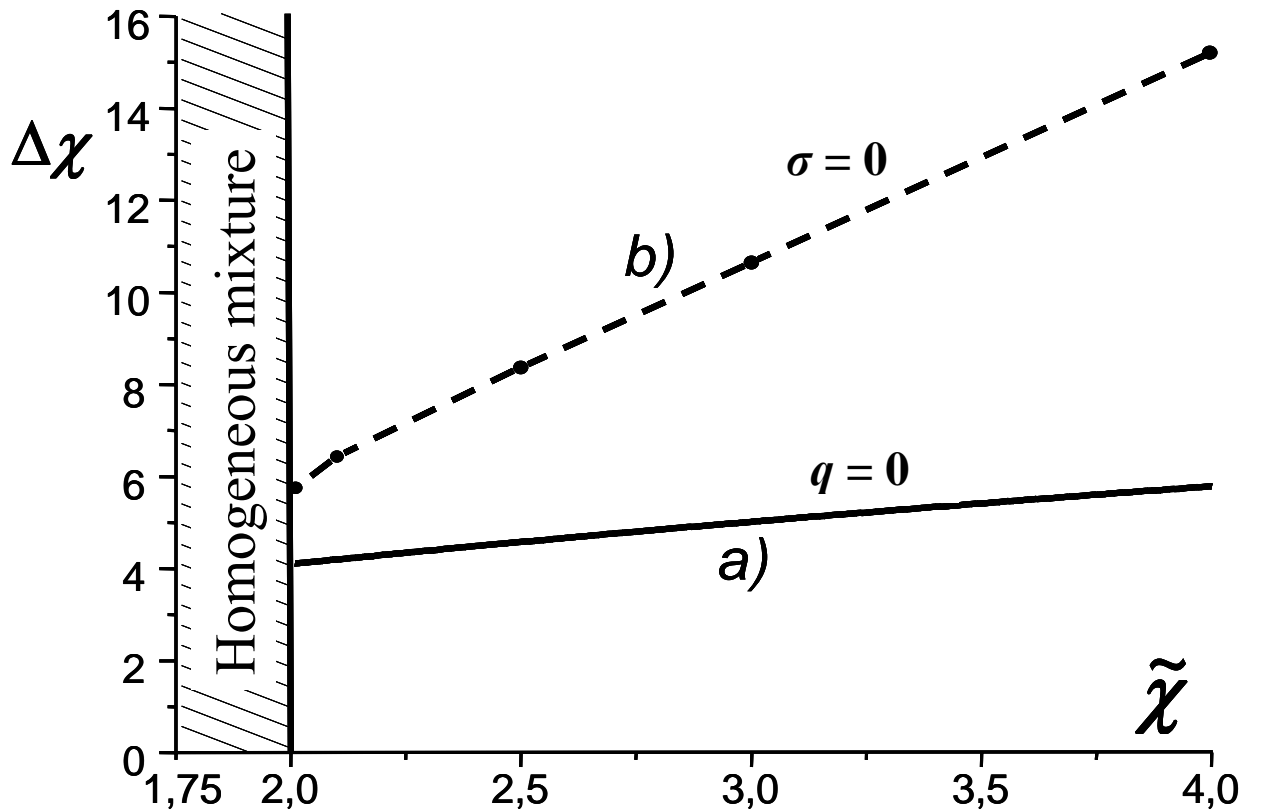

Figure 16. Phase diagram of the IL/nIL mixture in the coordinates ($\widetilde{\chi}$, $\Delta\chi$) at $\chi_{+-} = 0$, $u = 2$. *a*) The lower boundary of the domain of the possible mixture microphase separation described by the expression 4.14. *b*) The lower boundary of the domain of the mixture microheterogeneous state obtained in the chapter 3.

the same coordinates (see figure 13). The curve *a)* is the lower boundary of the domain in which microphase separation is possible. This curve is described by the equation 4.14. The curve *b)* is the lower boundary of the domain corresponding to the microhetrogeneous state of the mixture, which has been obtained in the chapter 3 by means of the phase boundary surface energy calculation. If $\widetilde{\chi} < 2$, the mixture is in the homogeneous state. This corresponds to the domain of the phase diagram which is located on the left of the vertical curve.

(In fact, the microphase separation is possible also at values of $\widetilde{\chi}$ that are a bit less than 2, since the microphase separation spinodal curve lies a bit lower than the macrophase separation spinodal curve, as it can be seen in the figure 15. But the domain located on the left of the vertical curve and also corresponding to the possible microphase separation of the mixture is not presented on the phase diagram of the figure 16, because it is very narrow.)

So, one can see that the results obtained in the present chapter and in the previous one are in qualitative agreement. Namely, in the both chapters by means of two different methods the following has been found out. If the value of the parameter $\widetilde{\chi}$ characterizing affinity of a nIL and an IL exceeds 2 then these two substances can form a microheterogeneous mixture in the case if the value of the parameter $\Delta\chi$ characterizing difference in the affinities of the IL's anions and of the IL's cations to the nIL molecules exceeds a certain critical value $\Delta\chi^*$. This value is the higher the higher is the value of $\widetilde{\chi}$.

The possibility of microphase separation in a pure IL can be also investigated by means of the method described above. This subject is also of interest because possibility of microphase separation in a pure IL has been predicted in the computer simulation work [70]. In this case the fluctuations of the cations and of the anions volume fractions are not independent. They are connected via the relation $\delta\Phi_+(x) + \delta\Phi_-(x) = 0$ that follows from the condition of the IL incompressibility, and the value G is expressed as:

$$G = 2 - \chi_{+-} + \chi_{+-} \frac{\tilde{q}^2}{6} + \frac{8\pi u}{\tilde{q}^2} \qquad 4.15$$

(see the appendix 2, equation A2.15). The minimum of this expression can attain zero at a non-zero value of the wave vector modulus $\tilde{q}$. Formally, this means that a microphase separation can take place in the system.

In the considered case appearing of a microstructure is caused by counteraction first of the tendency of the cations and the anions to segregate and thus decrease the amount of energetically unfavorable mutual contacts and second, of the electrostatic field effect that tends to equalize the concentrations of the cations and the anions in the whole volume of the IL. Spatial period of the microstructure having the lowest free energy is determined by the compromise of the two factors. In the considered case the spinodal conditions expressed by the equations 4.7 take the following form:

$$\left(\tilde{q}^*\right)^2 = \sqrt{\frac{48\pi u}{\chi_{+-}}}, \quad 2 - \chi_{+-} + 4\sqrt{\frac{\pi u \chi_{+-}}{3}} = 0 \qquad 4.16$$

As one can see, it follows from the requirement that the spatial period of the possible microheterogeneous structure must not be too small ($\tilde{q}^* \ll 1$) the equalities 4.16 can be fulfilled only at a very small value of u, that is unattainable in reality. Thus, it follows from the present consideration that hypothetically a microphase separation could take place in a pure IL consisting of huge ions, but in real systems it is impossible. However, this is not in a direct contradiction with the results of the work [70], because therein another more complicated and more detailed model of an IL has been considered.

Let us briefly summarize the chapter 4. It has been demonstrated that the spatially homogeneous state of the IL/nIL mixture is not stable towards microphase separation if the difference of the IL's anions and the IL's cations affinities to the neutral molecules exceeds a certain threshold value. This threshold value is the larger the lower is the compatibility of the IL as a whole and the nonionic liquid.

This result is in agreement with the results obtained in the chapter 3. Besides, it has been demonstrated that in the framework of the utilized model a microphase separation is not possible in a pure IL.

5. Swelling of a microgel with immobilized carbon nanotubes in an Ionic Liquid.

The present chapter is devoted to the study of swelling of a microgel with immobilized carbon nanotubes in an IL. It is an extension of the previous two chapters main idea for the case when a gel network acts as the second component in the system instead of a nIL. The investigation is focused again on the influence of the Van der Waals interactions of the system's components on the state of the system. Namely, it is supposed that the contact interactions of an IL's cations and anions with the gel network are different. This contact interactions difference leads to the break in the local equality of the cations and the anions concentrations inside the gel. The latter, in its turn, causes the predicted phenomenon, which lies in the fact that a smaller gel particle can be in the collapsed state while a larger gel particle having the same composition can be in the swollen state in the same IL.

5.1 The model of the system.

In more detail, the following model of the system is considered. As in the previous chapters a lattice model is utilized, in which it is supposed that the cations and the anions of the IL are spheres of the same diameter a. The behavior of a single particle of entangled by carbon nanotubes gel immersed in an IL is investigated (for short the words **gel** or **microgel** are used in the text below to denote a **gel particle**). It is supposed that the nanotubes are distributed uniformly over the gel and are arbitrarily oriented. The concentrations of the nanotubes in the gel is supposed to be high enough so that a percolation cluster is formed by them. Hence, it is supposed that the whole volume of the gel is entangled by a network of conductor, and this is the very reason why the carbon nanotubes have been introduced in the model.

It is supposed that the concentration of the nanotubes in the gel is low enough, so that they do not contribute to the elasticity of the gel and the simple well-known

expression [83] can be used for the description of the gel's network deformation free energy F^{el}:

$$\frac{F^{el}}{kT} = \frac{3}{2}M\left((\alpha)^2 + \left(\frac{1}{\alpha}\right)^2\right)$$

5.1

where M is the total number of the gel's subchains, and α is the gel's swelling ratio which relates the polymer volume fraction in the swollen gel, Φ_{gel}, with the fraction in the gel in the reference state, Φ_{gel}^0, in the following way:

$$\Phi_{gel} = \Phi_{gel}^0 / \alpha^3$$

5.2

The reference state of the gel is the state in which its subchains have the Gaussian size.

Let us introduce the Flory-Huggins parameters χ_{+-}, χ_{+}, χ_{-} which characterize the Van der Waals interactions respectively of the cations with the anions, of the cations with the gel network, and of the anions with the gel network. The meaning of these parameters is represented schematically in the figure 17. Let us also introduce the parameter $\tilde{\chi}$ that characterizes affinity of the IL as a whole to the gel network. This parameter is related with the parameters χ_{+-}, χ_{+}, χ_{-} via the same expression as the one used in the chapter 3 to relate the similarly denoted parameters (see eq. 3.4).
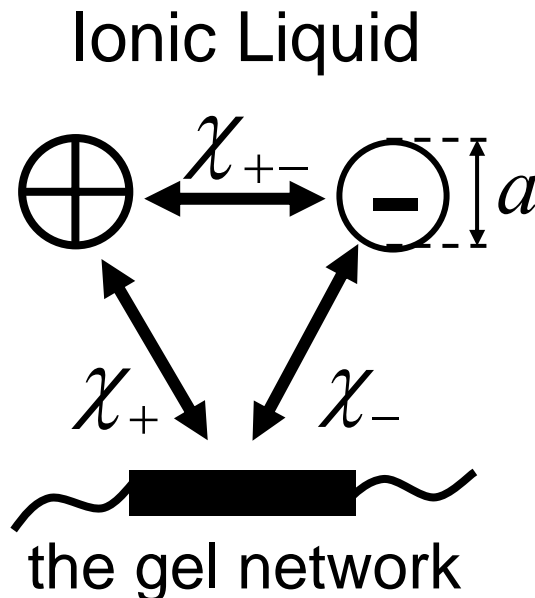

Figure 17. Schematic diagram representing parameters used for description of the Van der Waals interactions in the system.

It is supposed for definiteness, that the affinity of the anions to the gel network is higher than the affinity of the cations, i.e. $\chi_+ > \chi_-$. As a consequence, because the anions are attracted to the gel network stronger than the cations, concentration of the anions inside the gel turns out to be a bit higher than the concentration of the cations, i.e. a number of uncompensated anions appear inside the gel.

An electrostatic field can't appear in the volume entangled by a network of conductor. Therefore, each of the uncompensated anions is screened by the charge induced on the network. Hence, the uncompensated anions do not repel each other and, for this reason, they are spread uniformly over the volume of the gel. The charge opposite to this screening charge is distributed over the ends of the nanotubes at the surface of the gel. Charge of the gel is equal to the total charge of the uncompensated anions inside it.

An IL is an electrolyte with uppermost possible volume fraction of ions. For this reason, any charge located inside an IL is screened by an oppositely charged shell of uncompensated ions of the IL. Therefore the produced by the uncompensated anions charge of the gel is screened by a shell containing uncompensated cations. Because of a very high concentration of ions in an IL it is hard to describe the variation of ions concentration in the screening shell. For example, the Debye-Hückel approach is not applicable in this case. That's why we just suppose that the uncompensated cations are spread uniformly over the screening envelope (shell) of the gel. Total charge of the gel and the shell is equal to zero. The boundaries between the gel and the shell, and between the shell and the outer solution (pure IL) are sharp. In the outer solution cations and anions are compensated and their volume fractions are equal.

The model of the system is presented schematically in the figure 18. The black curves represent the polymer network of the gel and the network formed by carbon nanotubes in common. The uncompensated cations and anions are represented by
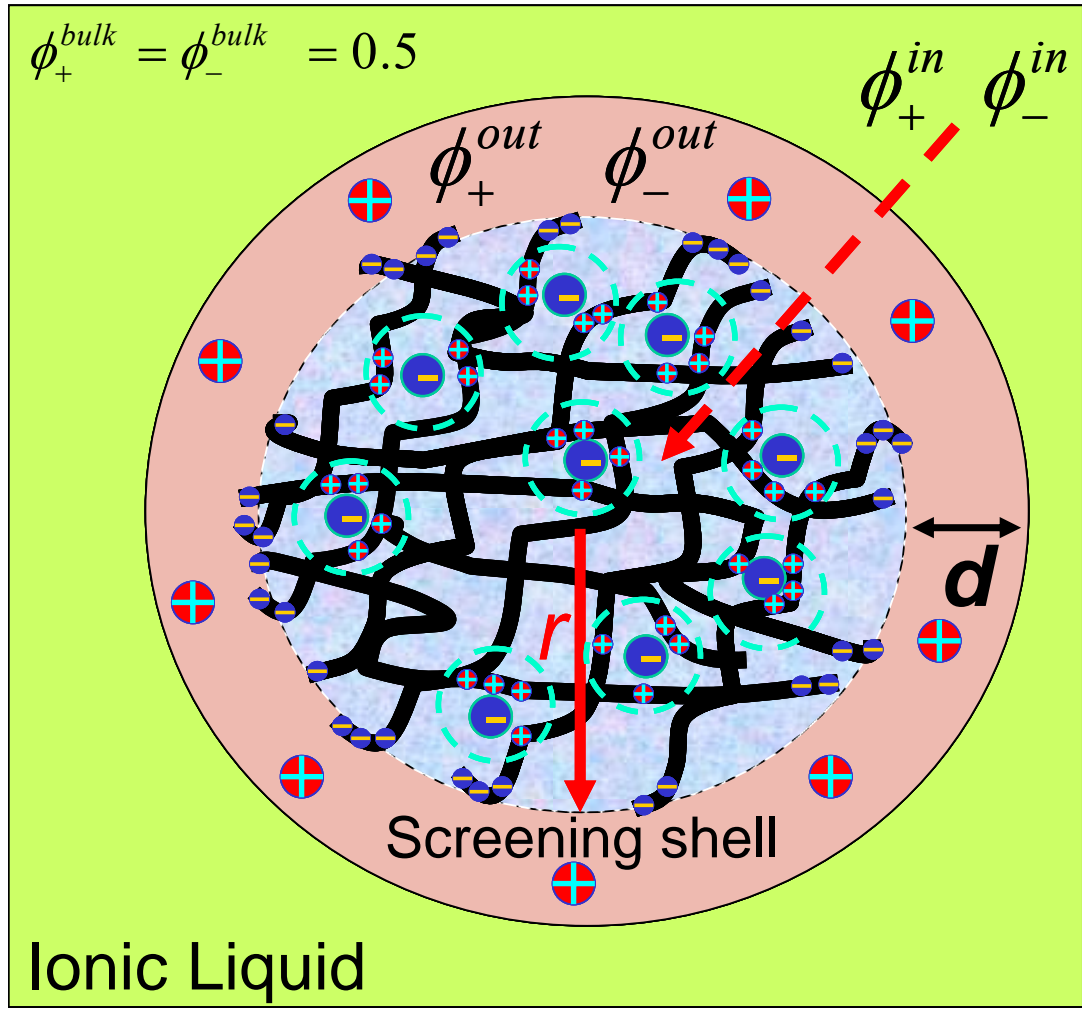
Figure 18. The schematic illustration of the considered model of the microgel with immobilized carbon nanotubes immersed in an ionic liquid. Black curves represent simultaneously the polymer network of the gel and the conducting network formed by the carbon nanotubes.

spheres (large ones) marked with the corresponding signs. The compensated ions are not depicted. The charges induced on the network of carbon nanotubes are represented by the small spheres marked with the corresponding signs.

Let us briefly set out the main idea of the predicted phenomenon. Hypothetically, if concentrations of the cations and the anions in all the points of the system were always same, then the gel would behave in the IL as in a normal one-component solvent interaction of which with the gel network is characterized by the parameter $\tilde{\chi}$. (The same statement for the mixture of an IL and a nIL has been

explained in the chapter 3). If the subchains of the gel are stiff enough, then the dependence of the gel swelling ratio α on the parameter $\tilde{\chi}$ would be like the one presented in the figure 19 (curve *a)*). When $\tilde{\chi}$ exceeds some certain threshold value $\tilde{\chi}_{thr}$, the gel collapses. The two states of the gel corresponding to the value $\tilde{\chi}_{thr}$ possess the same free energies. This dependence would be valid for any sample of the gel independently of the number of subchains it consists of.

But in reality, if the anions of the IL have a higher affinity to the gel network than the cations, the concentrations of the cations and of the anions are different in the gel, as it has been already mentioned. As a result, the free energy of the system is less than in the case of equal concentrations. The higher is the density of the gel
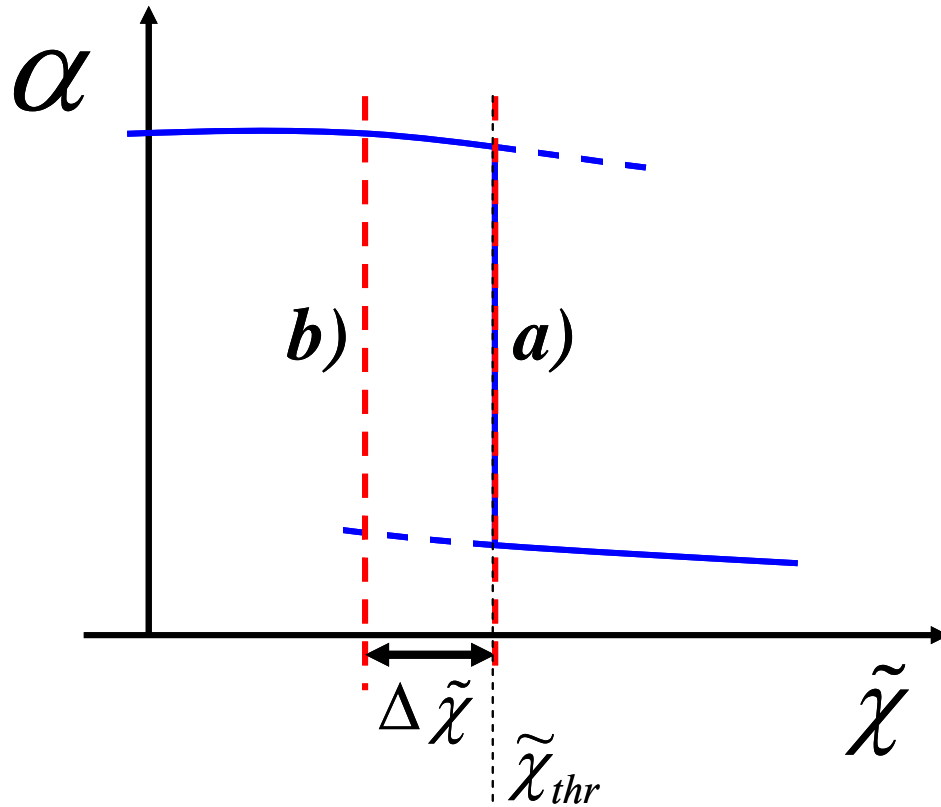

Figure 19. Dependence of the swelling ratio α of a microgel with immobilized carbon nanotubes immobilized in an IL on its affinity to the IL as a whole characterized by the parameter $\tilde{\chi}$. (*a*) In the hypothetical case when the cations and the anions of the IL can't segregate. (*b*) In reality.

network inside the gel, the stronger is the violation of the concentrations equality and the larger is the decrease of the system free energy as compared to the case of equal concentrations. Thus, equality of the system free energies in the two states corresponding to $\widetilde{\chi}_{thr}$ is broken. Namely, the collapsed state happens to be more energetically favorable. This means that the value of the parameter $\widetilde{\chi}$, at which in reality the collapsed and the swollen states of the gel are in equilibrium is less by a value of $\Delta\widetilde{\chi}$ than $\widetilde{\chi}_{thr}$ (see figure 19, curve *b)*).

Segregation of the cations and the anions is counteracted by electrostatic field appearing in the screening shell of the gel. Decrease of the total system free energy with increase of the anions concentration inside the gel is due to decrease of the part of the free energy corresponding to the contact Van der Waals interactions. The latter decrease is roughly proportional to the concentration of the uncompensated anions inside the gel and to the volume of the gel. On the other hand, if the concentration of the uncompensated anions inside the gel is fixed, the divided by the gel's volume energy of the electrostatic field grows with the growth of the volume. Hence, the larger is the gel, the stronger is the influence of the electrostatic field appearing due to the oppositely charged ions segregation and the less is the equilibrium concentration of uncompensated anions inside the gel.

This means that the larger is the number of subchains in a gel, the smaller is the shift $\Delta\widetilde{\chi}$ of the $\widetilde{\chi}$ threshold value from the value $\widetilde{\chi}_{thr}$ corresponding to the case of a normal one-component solvent. If the gel is very large then the electrostatic field completely prevents any segregation of oppositely charged ions inside the gel, and the gel behaves in the IL as in a normal one-component solvent, i.e. $\Delta\widetilde{\chi} = 0$.

An interesting fact follows from the foregoing speculations. Namely, if the value of the parameter $\widetilde{\chi}$ which describes affinity of the gel network to the IL as a whole is a bit less than the value $\widetilde{\chi}_{thr}$ at which the gel would collapse in a normal one-component solvent, then the state of the gel depends on the number of subchains it consists of.

Now let us present the idea in a more rigorous way with using formulas and figures. In the considered model the system consists of, so to say, three zones: the gel, the screening shell, and the outer solution. The three zones are spatially homogeneous. The free energy F^{tot} of the system comprises the electrostatic field energy $F^{el\text{-}st}$, the entropic contribution F^{ent}, the contribution F^{int} caused by Van der Waals interactions, the surface energy F^{surf}, and of gel network deformation energy F^{el} which has been already described (see eq. 5.1).

The uncompensated electrostatic charge is present at the ends of the carbon nanotubes at the surface of the gel, and in the screening shell. In fact, with relation to electrostatics, the system is a uniformly charged sphere of the radius r (the radius of the gel) that is surrounded by an oppositely uniformly charged spherical shell (the screening shell of the gel), having the thickness d. Energy of electrostatic field in such a system is equal to:

$$\frac{F^{el-st}}{kT} = q^2 u \frac{a}{2r} \frac{\omega^6}{\left(\omega^3 - 1\right)^2} \left[1 - \frac{1}{\omega} + \frac{1}{5}\frac{\omega^5 - 1}{\omega^6} - \frac{\omega^2 - 1}{\omega^3} \right] \qquad 5.3$$

where the parameter u is the one that has been first introduced in the chapter 3 (see eq. 3.9), ω is the ratio of the outer shell radius to the gel radius $\omega = (r + d)/r$, and q is the normalized to the elementary charge e total charge of the gel (of the sphere), which is equal to:

$$q = \frac{4}{3}\pi\Phi\frac{r^3}{a^3} \qquad 5.4$$

where Φ is the volume fraction of uncompensated anions inside the gel.

The entropic contribution to the free energy is caused by the translational motion of the cations and the anions and in the framework of the lattice model it is expressed in the ordinary way:

$$\frac{F^{ent}a^3}{kT} = \frac{4}{3}\pi r^3 \left(\phi_+^{in} \ln \phi_+^{in} + \phi_-^{in} \ln \phi_-^{in} \right) +$$
$$+ \frac{4}{3}\pi r^3 (\omega^3 - 1)\left(\phi_+^{out} \ln \phi_+^{out} + \phi_-^{out} \ln \phi_-^{out} \right) - \left(V - \frac{4}{3}\pi r^3 \omega^3 \right)\ln 2 \qquad 5.5$$

where the multipliers before the three terms containing logarithms are the volumes of the gel, the shell, and the outer solution, respectively. V is the whole volume of the system, which is a constant value and, hence, the comprising it term can be excluded. The last multiplier ln 2 in the expression 5.5 has appeared because the volume fractions of the cations and the anions in the outer solution are equal to 0.5. ϕ_+^{in}, ϕ_-^{in} and ϕ_+^{out}, ϕ_-^{out} are the volume fractions respectively of the cations and of the anions in the gel and in the shell. Due to the conditions of the solution incompressibility and of the total electroneutrality of the gel and the shell these volume fractions are related with the variables Φ and ω via the following equations:

$$\phi_+^{in} = \left(1 - \Phi_{gel} - \Phi\right)\big/2 \qquad \phi_-^{in} = \left(1 - \Phi_{gel} + \Phi\right)\big/2$$

$$\phi_+^{out} = \frac{1}{2} + \frac{\Phi}{2(\omega^3 - 1)} \qquad \phi_-^{out} = \frac{1}{2} - \frac{\Phi}{2(\omega^3 - 1)} \tag{5.6}$$

In a similar way, the contribution of the Van der Waals interactions to the free energy of the system is expressed as:

$$\frac{F^{int} a^3}{kT} = \frac{4}{3}\pi r^3 \left(\chi_{+-}\phi_+^{in}\phi_-^{in} + \chi_+\phi_+^{in}\Phi_{gel} + \chi_-\phi_-^{in}\Phi_{gel}\right) +$$

$$+ \frac{4}{3}\pi r^3 (\omega^3 - 1)\chi_{+-}\phi_+^{out}\phi_-^{out} + \left(V - \frac{4}{3}\pi r^3\omega^3\right)\chi_{+-}/4 \tag{5.7}$$

The last contribution to the system free energy is the surface free energy F^{surf}. It should be allowed for since there are two interfaces in the considered model: between the gel and the screening shell and between the shell and the outer solution. The interfaces are supposed to be infinitely thin.

In this case the surface energy can be calculated within the framework of the lattice approach in the following way. Let us suppose that there are two neighboring volumes of mixtures. Each mixture consists of the same N different enumerated components and the volume fractions of the i-th component in the first and in the second volume are equal to ϕ_1^i, ϕ_2^j, respectively. Let us imagine that the whole volume of the system is divided into elementary cells and each of them contains one

molecule of a component. Let us denote as J^{ij} the interaction energy of two adjacent cells in the case if the molecules of the components i and j are located inside these cells. Let us suppose that the interface is flat and S is its area.

The energy of interaction of adjacent cells that belong to the two different phases, i.e. the energy of contacts within the interface, is:

$$E_{pq} = \frac{S}{a^2} \sum_{i=1}^{N} \sum_{j=1}^{N} J^{ij} \phi_p^i \phi_q^j \qquad 5.8$$

where $p \equiv 1$, $q \equiv 2$. The contact of the two different mixtures can be produced for example in the following way. Two volumes of the two different mixtures are divided by a plane in two parts each. After that the two parts of the first type are brought in contact with the two parts of the second type. This means that with origination of the contact between the two different mixtures two other contacts between similar mixtures terminate. Area of each of the terminated contacts is two times less than the area of the originated contact. Hence, the energy of the phase boundary is:

$$E_{surf} = E_{pq}\Big|_{p\equiv1,q\equiv2} - \frac{1}{2} E_{pq}\Big|_{p\equiv1,q\equiv1} - \frac{1}{2} E_{pq}\Big|_{p\equiv2,q\equiv2} \qquad 5.9$$

Finally, with the help of the equation A1.8 relating the Flory-Huggins parameters and the energies J^{ij} the expression 5.9 can be transformed into the following one:

$$\frac{E_{surf}}{kT} = \frac{S}{6a^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \chi_{ij} \left(\phi_1^i \phi_2^j - \frac{1}{2} \phi_1^i \phi_1^j - \frac{1}{2} \phi_2^i \phi_2^j \right) \qquad 5.10$$

where χ_{ij} are the Flory-Huggins parameters describing the Van der Waals interactions of the i-th and the j-th components. With the help of the equation 5.10 one can obtain the expression describing the surface energy in the considered system:

$$\frac{F^{surf}}{kT} = \frac{2\pi r^2}{3a^2} \Big[\chi_+ \Phi_{gel} (\phi_+^{out} - \phi_+^{in}) + \chi_- \Phi_{gel} (\phi_-^{out} - \phi_-^{in}) + \qquad 5.11$$

$$\chi_{+-} (\phi_+^{in} \phi_-^{out} + \phi_-^{in} \phi_+^{out} - \phi_+^{out} \phi_-^{out} - \phi_-^{in} \phi_+^{in}) + \omega^2 \chi_{+-} (0.25 - \phi_+^{out} \phi_-^{out}) \Big]$$

The independent variables determining the state of the gel are α, Φ, and ω. The independent parameters characterizing the system are the already introduced Φ_{gel}^{0} (see eq. 5.2), u (see eq. 5.3), $\tilde{\chi}$, χ_{+-} and also the parameters $\Delta\chi$, Nv/a^3, and r_0/a.

The parameter $\Delta\chi$ represents the difference in affinities of the IL's anions and the IL's cations to the network of the gel and is related with the parameters χ_+ and χ_- via the same expression as the one used in the chapter 3 to relate the similarly denoted parameters (see eq. 3.19). The parameter Nv/a^3 is the normalized to a^3 volume of one gel's subchain. The volume of a subchain is the product of the number N of elementary units the subchain consists and the volume v one unit. The last parameter r_0/a is the ratio of the gel's radius in the reference state to the size a of an elementary cell. Let us identify r_0 shortly as **reference-state radius**. In the considered model this parameter characterizes the size of the gel. In order not to overcomplicate the treatment with minor parts the parameter χ_{+-} is supposed to be equal to zero everywhere in the present chapter.

At the given set of the system parameters the three variables determining the state of the system, were found by means of the free energy numerical minimization. As it has been mentioned, such a set of parameters has been chosen at which the gel is close to the swelling-collapse transition ($\tilde{\chi}$ is a bit less than $\tilde{\chi}_{thr}$). This means that at the considered values of parameters the free energy has two minima corresponding to two different sets (α, Φ, ω). Therefore, after the numerical search of the minima the one corresponding to the lowest value of the free energy has been chosen. The two different values of α correspond to the collapsed and to the swollen states of the gel.

While the numerical calculations a simplification has been introduced. Namely, it has been noticed in the course of the calculations that at the minimum of the system's free energy either the thickness d of the screening shell is less than the

diameter a of an ion or the value of ω is almost equal to the minimal value $(1+\Phi)^{1/3}$ at which the shell is composed of cations only.

First case is most frequent and it obviously has no physical meaning. In this case such a value of ω was taken that the value of d was exactly equal to a. In reality, this corresponds to a number of uncompensated cations that are spread over the surface of the gel not closely to each other and screen the gel's charge. In the second case it was supposed in the course of the calculations that the volume fraction of cations in the shell is exactly equal to unity and ω is equal to $(1+\Phi)^{1/3}$. Thus the value of ω was uniquely determined by the value of Φ.

Let us give an analytical corroboration of the aforementioned approximation. Let us find the equilibrium value of ω corresponding to some fixed values of α and Φ in the case when the screening shell composed of cations only has the thickness larger than a. Let us suppose that:

$$\omega = 1 + \Delta \equiv 1 + \frac{1}{3}\Phi + \Delta_2 \qquad\qquad 5.12$$

where Δ_2 is a value that is much less than Φ. Later on, we will prove that. As our numerical calculations have shown the volume fraction Φ of the uncompensated anions inside the gel is small and, hence, Δ is small. Therefore the energy of electrostatic field (see eq. 5.3) can be expanded into series of the value Δ powers and only the highest order term can be left:

$$\frac{F^{el-st}}{kT} = \frac{8}{27}\pi^2 \frac{r^5}{a^5} u \Phi^2 \Delta \qquad\qquad 5.13$$

With taking into account that Φ is small and Δ_2 is much smaller than Φ one can obtain by means of an expansion that the depending on Δ_2 part of the free energy corresponding to the gel-shell interface is approximately equal to:

$$\frac{\Delta F^{surf}_{\Delta_2}}{kT} = -2\pi \frac{r^2}{a^2} \Delta\chi \Phi_{gel} \frac{1}{\Phi} \qquad\qquad 5.14$$

The last depending on the value Δ_2 part of the free energy is the one corresponding to the ions entropy in the shell. By means of the same procedure one can obtain that

it is approximately equal to:

$$\frac{\Delta F^{ent-shell}}{kT} = 2\pi \frac{r^3}{a^3} \Delta \frac{\Delta_2}{\Phi} \left(\ln\left(\frac{3}{2} \frac{\Delta_2}{\Phi} \right) - 1 \right)$$ 5.15

Finally, after taking the derivative over Δ_2 of the sum of the expressions 5.13-5.15 and equating it to zero one can obtain the equilibrium value of Δ_2:

$$\frac{\Delta_2}{\Phi} = \frac{2}{3} \exp\left(\frac{\Delta\chi \Phi_{gel}}{\Phi\, r/a} - \frac{4}{27} \pi u \left(\frac{\Phi r}{a} \right)^2 \right)$$ 5.16

The parameter u is of order unity. Besides the inequality $\Phi r/a > 3$ is valid since the case is considered when all the screening uncompensated cations can't find room in a one-ion thick layer around the gel. In the swollen state the volume fraction Φ_{gel} is very low and therefore, as it follows from the equation 5.16, the ratio Δ_2 / Φ in this case is less than 0.02. So, it can be supposed that $\Delta_2 = 0$ what was to be proved.

Among the numerically investigated systems the collapsed gel ($\Phi_{gel} \approx 0.6$) at $\Delta\chi = 20$ and $\Phi = 3a/r$ corresponds to the maximum of the expression 5.16, which is equal to 0.6. Anyway, if one takes a bit larger value $\Phi_2 = 1.2 * 3a/r$ (i.e. the thickness of the shell composed of only the screening cations is $1.2a$ instead of a) then the expression 5.16 turns into 0.05 and Δ_2 can be supposed to be equal to zero. It is evident that the screening shell corresponding to $\Phi < \Phi_2$ is thinner than the one corresponding to Φ_2 but it can't be thinner than a. So, even if we suppose that $\Delta_2 = 0$ for a value of Φ that belongs to the interval $(3a/r; 1.2 * 3a/r)$ the obtained as a result of calculations value of d will differ from its actual value less than by 20%.

Same speculation concerns the case when the screening cations can't fill the one-ion thick layer. Namely, the thickness of the shell in this case is less than the thickness of the shell corresponding to the larger number of screening cations that can fill the layer completely. Since in the second case $d = a$ is an appropriate approximation it is to be appropriate in the first case as well.

5.2 The obtained results.

Results of our calculations for a system with a fixed set of the parameters Φ_{gel}^0, u, χ_{+-}, Nv/a^3 are presented in the figure 20. Let us explain its meaning. As it has been already mentioned a gel composed of a smaller number of subchains (and hence having smaller reference-state radius r_0) can be in the collapsed state in an IL while a gel of the same composition having a larger r_0 is in the swollen state in the same IL. Thus there exists the threshold value r_0^* of the reference-state radius demarcating the smaller gels that are to collapse and the larger gels that are to be swollen in the IL.
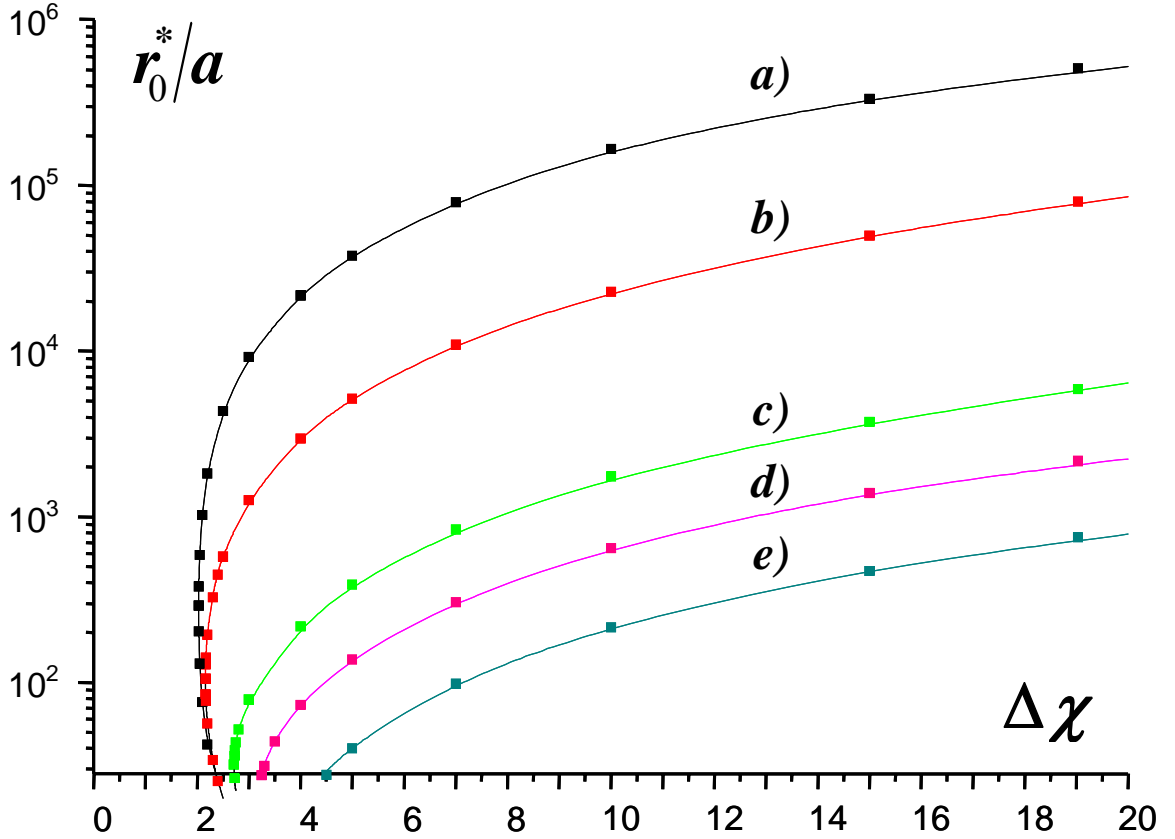

Figure 20. Dependence of the threshold value r_0^* of the microgel reference-state radius on the characterized by the parameter $\Delta\chi$ difference in affinities of the IL's anions and the IL's cations to the gel network. $\Phi_{gel}^0 = 0.003$, $Nv/a^3 = 100$, $u = 1$, $\chi_{+-} = 0$, $\tilde{\chi}_{thr} = 1.45964$ *a*) $\Delta\tilde{\chi} = 6.4*10^{-4}$ *b*) $\Delta\tilde{\chi} = 4.6*10^{-3}$ *c*) $\Delta\tilde{\chi} = 6.0*10^{-2}$ *d*) $\Delta\tilde{\chi} = 0.16$ *e*) $\Delta\tilde{\chi} = 0.46$. In the considered case number M of the gel's subchains is equal to one at $r_0 = 20a$.

The figure 20 represents the dependence of the threshold value r_0^* on the parameter $\Delta\chi$. Different curves correspond to the different values of $\Delta\widetilde{\chi}$. In other words the figure 20 is a phase diagram in the coordinates ($\Delta\chi$,r_0) which has the following physical meaning. Let us take for example the value of $\Delta\widetilde{\chi}$ equal to 0.06. If a point on the phase diagram is located below the curve *c)* then the gel, which has the corresponding reference-state radius r_0 will be in the collapsed state in the IL, so long as the difference in affinities of its cations and anions to the gel network is characterized by the corresponding value $\Delta\chi$. If the point is above the curve, then the gel will be in the swollen state in this IL. It follows from the figure 20 that if a synthesized sample of the gel is ground down and the obtained dispersion is immersed in an IL, it is possible that the smaller gel particles will collapse and the larger ones will be in the swollen state.

One can see in the figure that the higher is $\Delta\chi$, the larger is the maximal size of a collapsed gel. The maximal size of a collapsed gel also increases when $\widetilde{\chi}$ approaches the threshold value $\widetilde{\chi}_{thr}$ at which the gel would collapse in a normal one-component solvent.

With the help of the figure 20 it becomes evident why the word "microgel", and not just a "gel" stays in the title of the chapter. The radius of the gel is measured in diameters *a* of an ion. Since the average size of an IL's ions is rather large it can be supposed that *a* is of order one nanometer. One can see then in the figure that a normal threshold size of a gel between the collapsed and the swollen state is of order not higher than one micrometer. The predicted phenomenon most probably can be observed at small microscale gel sizes.

However if $\widetilde{\chi}$ is very close to $\widetilde{\chi}_{thr}$ the threshold value r_0^* can be rather large. In theory, if $\widetilde{\chi}$ tends to $\widetilde{\chi}_{thr}$, the maximal size of a collapsed gel tends to infinity. For example, in the case represented by the curve *a)* it reaches one millimeter. But it may be hard to find a corresponding system in reality. Let us also note that the

minimal reference state radius of the gel that has a physical meaning is the one at which the gel consists of only single subchain. For the case presented in the figure 20 this radius is equal to $\approx 20a$.

The figure 21 represents the dependence of threshold value r_0^* of the microgel reference-state radius on the value of $\tilde{\chi}$ at a fixed value of $\Delta\chi$. Actually, the figure repeats the data presented in the figure 20. In the figure one can see again that when $\tilde{\chi}$ approaches the threshold value $\tilde{\chi}_{thr}$ the maximal reference state radius r_0^* of the gel grows. It can be seen that it grows asymptotically.

It has been noticed that the product $r_0^* \Delta\tilde{\chi}$ is approximately constant. We have explained this fact analytically. The gel is considered that is close to the collapse-swelling transition. In fact, the swelling ratio of the gel in the considered swollen
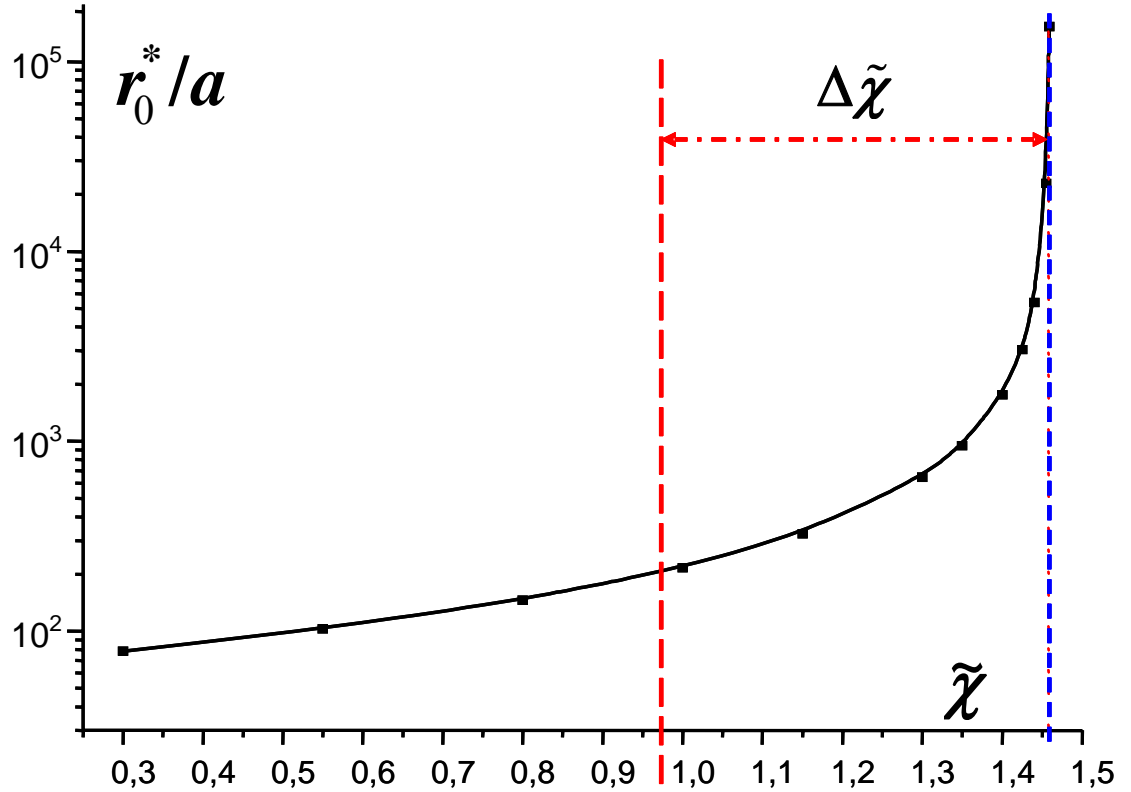

Figure 21. Dependence of the threshold value r_0^* of the microgel reference-state radius on the parameter $\tilde{\chi}$. $\Delta\chi = 10$, $\Phi_{gel}^0 = 0.003$, $Nv/a^3 = 100$, $u = 1$, $\chi_{+-} = 0$, $\tilde{\chi}_{thr} = 1.45964$. In the considered case number M of the gel's subchains is equal to one at $r_0 = 20a$.

87

state is close to the one the gel would have in the swollen state if the parameter $\Delta\chi$ were equal to zero. Same concerns the swelling ratio of the gel in its collapsed state.

In the swollen state the concentration of uncompensated anions inside the gel as well as the caused by it change of the system's free energy is much less than in the collapsed state, since the concentration of the gel chains inside the gel is much less in the swollen state than in the collapsed state. That's why, for simplicity let us take into account only the break in the cations and the anions concentrations equality that takes place in the collapsed state.

If $\Delta\chi = 0$ and $\tilde{\chi} = \tilde{\chi}_{thr}$ then the corresponding to the collapsed and the swollen states of the gel free energies are equal. If the parameter $\tilde{\chi}$ is changed by a small value $\Delta\tilde{\chi}$, then the difference of the free energies in the swollen and in the collapsed states becomes equal to:

$$\frac{\Delta F^{normal}}{kT} = \frac{4\pi r_0^3}{3a^3} \Delta\tilde{\chi} \left[\left(\Phi_{gel}^0\right)^2 \left(\frac{1}{\alpha_{col}^3} - \frac{1}{\alpha_{sw}^3} \right) + \left(p(\alpha_{col}) - p(\alpha_{sw}) \right) \right]$$

where

5.17

$$p(\alpha) = \frac{3\frac{\left(\Phi_{gel}^0\right)^2}{\alpha^4} \left[\alpha^2 \ln\left(1 - \frac{\Phi_{gel}^0}{\alpha^3} \right) + \frac{\Phi_{gel}^0}{\alpha} + \frac{\tilde{\chi}\left(\Phi_{gel}^0\right)^2}{\alpha^4} + \frac{\Phi_{gel}^0}{Nv/a^3}\left(\alpha - \frac{1}{\alpha^3} \right) \right]}{2\alpha \ln(1 - \frac{\Phi_{gel}^0}{\alpha^3}) + \frac{3\alpha\, \Phi_{gel}^0}{\left(\alpha^3 - \Phi_{gel}^0\right)} - \frac{\Phi_{gel}^0}{\alpha^2} - \frac{4\tilde{\chi}\left(\Phi_{gel}^0\right)^2}{\alpha^5} + \frac{\Phi_{gel}^0}{Nv/a^3}\left(1 + \frac{3}{\alpha^4} \right)}$$

In the equation 5.17 the first term in the square brackets appears due to the caused by the change of $\tilde{\chi}$ change of the energies of Van der Waals interactions in the swollen and in the collapsed states. The second term appears due to the caused by the change of $\tilde{\chi}$ change of the swelling ratios of the gel in the two states. For the considered by us system the second term is 10^4 times less than the first one and it can be neglected.

If the parameter $\Delta\chi$ becomes higher than zero, then uncompensated anions appear in a collapsed gel (for a swollen gel we don't take this into account) and it

also causes the change in its free energy. Namely, the energy of Van der Waals interactions inside the gel decreases by:

$$\frac{\Delta F^{int}}{kT} = \Phi^0_{gel} \frac{4}{3}\pi \frac{r_0^3}{a^3}\Phi\Delta\chi \qquad\qquad 5.18$$

The equivalence of the product $r_0^* \Delta\tilde{\chi}$ to a constant value is best fulfilled at large values of r_0^* and therefore, this case is considered. At large values of r_0^* the thickness of the screening shell is larger than a and, as it has been proved in the end of the section 5.1, it can be assumed in this case that the volume fraction of the cations in the screening shell is equal to unity. Hence, the appearing due to ions segregation increase of the free energy entopic part corresponding to the zone occupied by the screening shell is equal to:

$$\frac{\Delta F^{ent\_shell}}{kT} = \frac{4}{3}\pi\left(\omega^3 - 1\right)\frac{r^3}{a^3}\ln 2 = \frac{4}{3}\pi\Phi \frac{r_0^3}{a^3}\alpha^3_{col}\ln 2 \qquad\qquad 5.19$$

The volume fraction Φ of the uncompensated anions inside the gel is small. Therefore, the expression 5.13 can be used for the description of the electrostatic field energy (with substituting $\Delta_2 = 0$).

By means of expanding into series of the value Φ powers and leaving only the highest order term one can obtain that the decrease of the entropic contribution to the free energy caused by translational motion of ions inside the gel is equal to:

$$\frac{\Delta F^{ent-gel}}{kT} = \frac{2}{3}\pi \frac{r_0^3}{a^3}\alpha^3_{col}\frac{\Phi^2}{1-\Phi_{gel}} \qquad\qquad 5.20$$

Since large values of r_0 are considered, the contribution 5.20 is negligible as compared to the electrostatic contribution and can be omitted. The last contribution to the change of the system free energy is the one corresponding to the interface between the gel and the shell:

$$\frac{\Delta F^{surf}}{kT} = \frac{2}{3}\pi \frac{r_0^2}{a^2}\Delta\chi \frac{\Phi^0_{gel}}{\alpha_{col}}\left(1 + \Phi + \frac{\Phi^0_{gel}}{\alpha^3_{col}}\right) \qquad\qquad 5.21$$

If one now minimizes over Φ the composed of the contributions 5.13, 5.18, 5.19, 5.21 free energy corresponding to the collapsed state of the gel one can obtain the following expression for the equilibrium value of Φ:

$$\Phi^2 = \frac{9\left(\Phi_{gel}^0 \Delta\chi\left[1 - \dfrac{1}{2r_0\alpha_{col}}\right] - \alpha_{col}^3 \ln 2\right)}{2\pi r_0^2 \alpha_{col}^5 u} \equiv \frac{C}{r_0^2} \qquad 5.22$$

In the expression 5.22 the value C has been introduced. In the considered case of large values of r_0 the term of the expression 5.22 located in the square brackets which has r_0 in the denominator can be omitted. Then C doesn't depend on r_0.

After substituting this equilibrium value of Φ into the equations 5.13, 5.18, 5.19, 5.21 and taking into account the equation 5.17 one can get the following expression which describes the difference of the free energies corresponding to the collapsed and to the swollen states:

$$\frac{\Delta F}{kT} = \frac{4\pi r_0^3}{3a^3}\Delta\tilde{\chi}\left(\Phi_{gel}^0\right)^2\left(\frac{1}{\alpha_{col}^3} - \frac{1}{\alpha_{sw}^3}\right) + \frac{4\pi r_0^3}{3a^3}\frac{\sqrt{C}}{r_0}\left(\alpha_{col}^3 \ln 2 - \Phi_{gel}^0 \Delta\chi\right) +$$

$$+ \frac{8}{81}\pi^2 r_0^5 \alpha_{col}^5 u \frac{C\sqrt{C}}{r_0^3} + \frac{2}{3}\pi r_0^2 \Delta\chi \frac{\Phi_{gel}^0}{\alpha_{col}}\left(1 + \frac{\sqrt{C}}{r_0}\right) \qquad 5.23$$

Finally, after equating to zero this difference one can obtain the expression which relates the value of the parameter $\Delta\tilde{\chi}$ and the maximal reference state radius r_0^* of a collapsed gel:

$$r_0^* \Delta\tilde{\chi} = \frac{\dfrac{4}{27}C\sqrt{C}\pi\alpha_{col}^5 u - \dfrac{\Delta\chi}{2}\dfrac{\Phi_{gel}^0}{\alpha_{col}}}{\left(\Phi_{gel}^0\right)^2\left(\dfrac{1}{\alpha_{col}^3} - \dfrac{1}{\alpha_{sw}^3}\right)} \qquad 5.24$$

Thus it has been proven that at fixed values of the parameters Φ_{gel}^0, u, $\tilde{\chi}$, $\chi_{+-} = 0$, $\Delta\chi$, and Nv/a^3 the product $r_0^* \Delta\tilde{\chi}$ is a constant at large values of r_0^*. Comparison between some values of this product obtained by means of numerical calculations and by means the expression 5.24 is presented in the table 1.

Table1.

$\Delta\chi$	$\dfrac{r_0^*}{a}\Delta\tilde{\chi}$ numerical	$\dfrac{r_0^*}{a}\Delta\tilde{\chi}$ analytical
5	20	21.8
10	100	111
20	350	398

Let us summarize briefly the chapter 5. It has been demonstrated that the swelling ratio of an immersed in an IL microgel with immobilized carbon nanotubes depends on the microgel's size if there is a difference in affinities of the IL's anions and the IL's cations to the network of the microgel. If the affinity of the IL as a whole to the network of the microgel is a bit higher than the affinity at which the microgel would collapse if a one-component solvent were instead of the IL, then a smaller microgel can be in the collapsed state in this IL while a larger microgel is in the swollen state in this IL. Maximal size of a collapsed microgel increases with the increase of the difference in the affinities of the IL's anions and the IL's cations to the network of the microgel. Maximal reference-state radius of a collapsed microgel grows asymptotically as the affinity of the IL as a whole to the network of the microgel approaches the aforementioned value at which the microgel would collapse in a normal one-component solvent.

Conclusions.

In the present dissertation several phenomena related with ions equilibrium distribution in binary systems containing ILs have been theoretically considered. Mainly binary mixtures of an IL and a nonionic liquid have been investigated. Main results of the work are the following:

1. In the chapter 2 it has been demonstrated that the higher is the energy of an IL's cation and anion contact caused by their Van der Waals interaction, i.e. the stronger is their incompatibility, the stronger is the solvent power of this IL with respect to an arbitrary nonionic liquid.

2. In the chapter 3 the phase boundary between an IL and a nonionic liquid has been investigated. It has been found out that a double electrostatic layer is formed at the boundary and the electrostatic energy of the layer is the higher the higher is the difference in the affinities of the IL's cations and the IL's anions to the to the neutral molecules.

3. It has been also demonstrated in the chapter 3 that if an IL as a whole is poorly mixable with a nIL then the thickness of the phase boundary between them increases with the growth of the difference in the affinities of the IL's cations and the IL's anions to the neutral molecules. Vice versa, if the IL and the nIL are almost absolutely mixable the thickness of the phase boundary decreases.

4. The surface tension of the phase boundary between an IL and a nIL has been also calculated in the chapter 3 and it has been found out that the surface tension decreases with the increase of the compatibility of the nIL and the IL as a whole. The surface tension decreases also with the growth of the difference in the affinities of the IL's cations and the IL's anions to the neutral molecules.

5. It has been found out that if two volumes of an IL and a nIL can't form a homogeneous solution and if the difference in the affinities of the IL's cations

and the IL's anions to the molecules of the nIL is higher than a certain threshold value then formation of a microheterogeneous structure is possible in the IL/nIL mixture. The mentioned threshold value is the higher the lower is the compatibility of the IL and the nIL. This result has been obtained in the chapters 3 and 4 by means of two different methods. Namely, in the chapter 3 it has been obtained by means of calculation of the surface tension of the phase boundary between an IL and a nIL, and in the chapter 4 it has been obtained by means of investigating of the homogeneous IL/nIL mixture stability towards microphase separation.

6. In the chapter 5 it has been demonstrated that the swelling ratio of an immersed in an IL microgel with immobilized carbon nanotubes depends on it's size if there is a difference in affinities of the IL's anions and the IL's cations to the network of the microgel. If the affinity of the IL as a whole to the network of the microgel is a bit higher than the affinity of a one-component solvent to the network at which the microgel would collapse then a smaller micrgel is in the collapsed state in this IL and a larger microgel is in the swollen state in this IL. Maximal size of a collapsed microgel increases with increase of the difference in the affinities of the IL's anions and the IL's cations to the network of the microgel.

Acknowledgments.

Appendix 1.

Free energy of a ternary mixture molecules contacts in the case when there exists a gradient of the mixture's components concentrations.

In this section there is presented the derivation of the expression describing the free energy of contacts of a ternary mixture molecules for the general case when the mixture is not homogeneous, i.e. there exists a gradient of its components concentrations. It is supposed that molecules of all the components of the considered mixture are spheres of the same radius. The presented below derivation is a generalization of the derivation presented in the textbook [84] for the case of a binary mixture.

It is supposed that the whole volume of the mixture is composed of similar elementary cells, and each of them is occupied by a molecule of the type A, B or C. The cells are enumerated, and for each cell with a number i two variables p_i and q_i are introduced. The value of the variable p_i (q_i) is equal to unity if there is a molecule of the type A (B) in the cell, and otherwise it is equal to zero. If the both variables p_i and q_i are equal to zero, then the cell with the number i contains neither a molecule of the type A nor a molecule of the type B. This means that a molecule of the type C occupies this cell.

The interaction energy K_{ij} of two cells with the indexes i and j can be expressed as:

$$
\begin{aligned}
K_{ij} &= J_{ij}^{AA} p_i p_j + J_{ij}^{BB} q_i q_j + J_{ij}^{CC} (1-p_i)(1-p_j)(1-q_i)(1-q_j) + \\
&+ J_{ij}^{AC}\left[p_i(1-p_j)(1-q_j) + p_j(1-p_i)(1-q_i)\right] + \\
&+ J_{ij}^{BC}\left[q_i(1-p_j)(1-q_j) + q_j(1-p_i)(1-q_i)\right] + \\
&+ J_{ij}^{AB}(p_i q_j + p_j q_i)
\end{aligned}
\qquad \text{A1.1}
$$

where J_{ij}^{EF} denotes the interaction energy of the cells i and j in the case if the molecules of the types E and F are located inside them (E,F = A,B or C). It is

supposed here that the energy of two molecules interaction depends only on the location of the two molecules but depends nowise on the other molecules. The expression A1.1 is composed in such a manner that if the molecules of the types E and F are located in the cells i and j then the depending on the variables p_i, q_i, p_j, q_j part of the containing the multiplier J_{ij}^{EF} term turns into unity, and other terms of the expression A1.1 turn into zero.

Hence, for any pair of molecules E and F located in the cells i and j the expression A1.1 representing the energy of the two cells interaction is exactly equal to the energy of the two molecules interaction. This is as it should be. Each of the last three terms of the expression A1.1 comprises two summands that are invariant with respect to interchange of the indexes i and j. This is due to the fact that the energy of two molecules interaction is invariant with respect to their interchange. That is, each of the last three terms allows for the both configurations of the two molecules in the case if the molecules are of different types.

In any state of the system the total energy F_{int} of its molecules interaction is expressed as:

$$F_{\text{int}} = \left\langle \frac{1}{2} \sum_{i,j} K_{ij} \right\rangle$$

A1.2

where summation is carried out over all the cells of the system and the average is taken over all the microstates or, in other words, over all the molecules configurations corresponding to the given state of the system. The factor ½ is introduced into the expression A1.2 in order not to take an account of the same configurations of molecules twice. That happens necessarily when summation over two indexes is carried out.

To simplify the expression A1.1 for the further operations with it let us add to it and then subtract from it the term:

$$\left(J_{ij}^{AA} + J_{ij}^{BB}\right)p_i q_j + \left(J_{ij}^{AA} + J_{ij}^{CC}\right)p_i(1 - p_j)(1 - q_j) +$$
$$+ \left(J_{ij}^{BB} + J_{ij}^{CC}\right)q_i(1 - p_j)(1 - q_j)$$

A1.3

As a result, the energy K_{ij} of the cells i and j interaction can be expressed as a sum of the two following expressions:

$$K_{ij}^a =$$
$$= J_{ij}^{AA} \{p_i p_j + p_i q_j + p_i(1 - p_j)(1 - q_j)\} + J_{ij}^{BB} \{q_i q_j + p_i q_j +$$
$$+ q_i(1 - p_j)(1 - q_j)\} + J_{ij}^{CC} \{(1 - p_i)(1 - p_j)(1 - q_i)(1 - q_j) +$$
$$+ p_i(1 - p_j)(1 - q_j) + q_i(1 - p_j)(1 - q_j)\}$$

A1.4

and

$$K_{ij}^b =$$
$$= J_{ij}^{AB} \left(p_i q_j + p_j q_j\right) - \left(J_{ij}^{AA} + J_{ij}^{BB}\right) p_i q_j + J_{ij}^{AC} \{p_i(1 - p_j)(1 - q_j) +$$
$$+ p_j(1 - p_i)(1 - q_i)\} - p_i(1 - p_j)(1 - q_j)\left(J_{ij}^{AA} + J_{ij}^{CC}\right) +$$
$$+ J_{ij}^{BC} \left[q_i(1 - p_j)(1 - q_j) + q_j(1 - p_i)(1 - q_i)\right] -$$
$$- q_i(1 - p_j)(1 - q_j)\left(J_{ij}^{BB} + J_{ij}^{CC}\right)$$

A1.5

Let us now simplify the expression A1.4 by means of opening in it the brackets, collecting, and excluding the summands containing the multipliers $p_j q_j$ or $p_i q_i$, which are equal to zero because two different molecules of the types A and B can't be in the same cell simultaneously. As a result we obtain:

$$K_{ij}^a = J_{ij}^{AA} p_i + J_{ij}^{BB} (q_i + p_i q_j - p_j q_i) + J_{ij}^{CC} (1 - p_j - q_j)$$

A1.6

In the present consideration only contact interactions of molecules that are spherically symmetrical are taken into account. Hence, it is assumed that the interaction energy of the located in the cells i and j two molecules of the types E and F is equal to zero if the cells are not adjacent or coincide (a molecule can't interact with itself) and it is equal to a fixed constant value J^{EF} if the cells are adjacent.

Let us sum the value K_{ij} expressed as a sum of the expressions A1.5 and A1.6 over all the elementary cells and take the average of the result according to the expression A1.2. First let us sum the expression A1.6:

$$\sum_{ij} K_{ij}^a = 6J^{AA} \sum_i p_i + 6J^{BB} \sum_i q_i + 6J^{CC} \sum_i (1 - p_i - q_j) =$$
$$= 6J^{AA} N_A + 6J^{BB} N_B + 6J^{CC} (N - N_A - N_B)$$

A1.7

Where N is the total amount of elementary cells, N_A is the total amount of the molecules of the type A, and N_B is the total amount of the molecules of the type B in the system. After the first summation the appearing of the multiplier 6 in front of each term is due to the fact that each cell with the number i has 6 adjacent cells which give same contributions while the summation over the index j. As a system with an invariable volume and composition is considered, the expression A1.7 represents a constant value. Hence, this contribution to the free energy can be excluded while it is of no importance.

Before the summation of the expression A1.5 let us introduce in it the following substitutions for all the pairs of molecules of the types E and F (E,F = A,B or C):

$$\chi_{EF} = 6\left(J^{EF} - \frac{J^{EE} + J^{FF}}{2}\right)\bigg/ kT \qquad \text{A1.8}$$

where χ_{EF} is the Flory-Huggins parameter characterizing the contact interaction of the two molecules of the types E and F. The factor, reciprocal to the temperature T and the Boltzmann constant k, is introduced in the expression A1.8 to make the parameter χ_{EF} dimensionless. Again after excluding the terms containing the multipliers $p_j q_j$ or $p_i q_i$ and taking into account that terms invariant with respect to interchange of the indexes i and j produce the same result after summation, one obtains:

$$\frac{F_{int}}{kT} = <\sum_{ij(i)} \frac{1}{6}\left\{\chi_{AB}\, p_i q_j + \chi_{AC}\left(1 - p_j - q_j\right)p_i + \chi_{BC}\left(1 - p_j - q_j\right)q_i\right\}> \qquad \text{A1.9}$$

where summation over the first index i is carried out over all the cells of the system and summation over the second index j is carried out over the six cells that are adjacent to the cell with the given index i. In the expression A1.9 the terms linear in p_i or in q_i can be excluded because they produce a constant contribution to the free energy. As to the terms comprising product of the variables p and q having different indexes i and j, they can be transformed in the following way:

Let us denote as *x, y, z* the coordinates of the center of the elementary cell having index *i*. Then, for example, the first term of A1.9, in which the constant factor $\chi_{AB}/6$ has been temporarily omitted, can be transformed as follows:

$$
\begin{aligned}
<\sum_{ij(i)} p_i q_j > = \frac{1}{a^3} \int_V d^3r \Big[&\Phi_A(x, y, z)\{\Phi_B(x+a, y, z)+ \\
&+\Phi_B(x-a, y, z)+\Phi_B(x, y+a, z)+\Phi_B(x, y-a, z)+ \\
&+\Phi_B(x, y, z+a)+\Phi_B(x, y, z-a)\}\Big]
\end{aligned}
\qquad \text{A1.10}
$$

where Φ_A and Φ_B are the volume fractions of the components A and B, respectively, in the points of the system, coordinates of which are indicated in the round brackets, and *a* is the length of an elementary cubic cell edge (a^3 is the volume of the cell).

To obtain the expression A1.10 first summation over the index *j* has been carried out, i.e. all the six summands enumerated by the index *j* that are produced by the cells adjacent to the cell with the index *i* have been explicitly written. After that, averaging of each summand has been performed with taking into account that the variables *p* and *q* with different indices are independent and, hence, an average of their product is the product of their averages. It has been also taken into account that averages of the variables p_i and q_i are nothing else but the volume fractions of the components A and B, respectively, in the point of the system where the center of the cell with the index *i* is located. At last, a transition from summation over all the elementary cells to integration over the whole volume *V* of the mixture has been performed.

The last transformation implies that spatial variations of concentrations in the considered system are smooth, and the characteristic spatial scale of the variations is significantly larger than the size *a* of an elementary cell. If one assumes this, besides an approximate equality that connects the volume fractions of components in the adjacent cells can be used. Namely, expansion into the Taylor series can be done, and only the two terms of the highest order can be left in it. For example:

$$\Phi_B(x-a,y,z)+\Phi_B(x-a,y,z)\cong 2\Phi_B(x,y,z)+a^2\frac{\partial^2\Phi_B(x,y,z)}{\partial x^2} \quad \text{A1.11}$$

By means of applying the transformation expressed by the equation A1.11 to the summands of the expression A1.10 the latter one can be transformed to:

$$\frac{1}{a^3}\int_V d^3r\left[\Phi_A(x,y,z)\left\{6\Phi_B(x,y,z)+a^2\Delta\Phi_B(x,y,z)\right\}\right] \quad \text{A1.12}$$

Let us transform the second term of the expression A.12 after temporarily omitting its constant factor $1/a$:

$$\int_V d^3r\Phi_A(x,y,z)\Delta\Phi_B(x,y,z)=$$

$$=\int_V d^3r\vec{\nabla}\left(\Phi_A(x,y,z)\vec{\nabla}\Phi_B(x,y,z)\right)-\int_V d^3r\vec{\nabla}\Phi_A(x,y,z)\vec{\nabla}\Phi_B(x,y,z) \quad \text{A1.13}$$

Finally, in the expression A1.13 the first term is equal to zero because:

$$\int_V d^3r\vec{\nabla}\left(\Phi_A(x,y,z)\vec{\nabla}\Phi_B(x,y,z)\right)=\int_S d\vec{S}\Phi_A(x,y,z)\vec{\nabla}\Phi_B(x,y,z)=0 \quad \text{A1.14}$$

where in the right part of the equation the integration is performed over an envelope surface of the considered system.

As a result, after applying the described above procedure (see expressions A1.10-A1.14) to all the summands of the expression A1.9 and returning all the temporarily omitted constant factors one can obtain the following expression which describes the free energy that corresponds to contacts of a ternary mixture molecules:

$$\frac{F_{int}}{kT}a^3=\int_V d^3r\left[\chi_{AB}\Phi_A\Phi_B+\chi_{BC}\Phi_B\Phi_C+\chi_{AC}\Phi_A\Phi_C-\right.$$

$$\left.-\frac{a^2}{6}\left(\chi_{AB}\vec{\nabla}\Phi_A\vec{\nabla}\Phi_B+\chi_{AC}\vec{\nabla}\Phi_A\vec{\nabla}\Phi_C+\chi_{BC}\vec{\nabla}\Phi_B\vec{\nabla}\Phi_C\right)\right]+const \quad \text{A1.15}$$

Appendix 2.

Increment of the free energy of a homogeneous mixture of an ionic liquid and a nonionic liquid caused by a fluctuation of the components concentrations.

In this section there is presented the derivation of the expression describing the increment of the IL/nIL homogeneous mixture free energy which appears due to the origination in the mixture of a small deviation of the components concentrations from their average values. The components concentrations fluctuations (their deviations from the average values) are expressed by the equations 4.1 - 4.3. As a special case, there is considered the increment of the free energy of a pure IL appearing due to a small fluctuation of the cations and the anions concentrations. The notations which are not explained in the present section are taken from the chapters 2, 3, and 4.

Let us perform a transition into the reciprocal Fourier space. Namely, instead of dealing with different functions depending on the coordinates of a mixture point described by the vector $\boldsymbol{r}$ let us deal with their Fourier transforms which are functions of the coordinates of a located in the reciprocal Fourier space point that is described by the wave vector $\boldsymbol{q}$. A function $\varphi(\boldsymbol{r})$ (let us take, as an example, the potential of the electrostatic field) and its Fourier transform $\varphi^q(\boldsymbol{q})$ are connected via the equations:

$$\varphi^q(\boldsymbol{q}) = \int_V (2\pi)^3 \, d^3\boldsymbol{r} \exp(-i\boldsymbol{q}\boldsymbol{r})\varphi(\boldsymbol{r}) \quad \varphi(\boldsymbol{r}) = \int \frac{d^3\boldsymbol{q}}{(2\pi)^3} \exp(i\boldsymbol{q}\boldsymbol{r})\varphi^q(\boldsymbol{q}) \quad \text{A2.1}$$

In the first equation of A2.1 the integration is performed over the whole volume of the mixture, which is supposed to be infinite, though. The integration in the second equation of A2.1 is performed over the whole reciprocal Fourier space.

The density of electrostatic charge that appears in an arbitrary point $\boldsymbol{r}$ of the mixture as a result of the concentrations fluctuations is equal to:

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

<div align="right">A2.2</div>

(see for comparison the expression 3.5).

Electrostatic field energy of the mixture is expressed in terms of the electrostatic charge density $\rho(r)$ and the electrostatic field potential $\varphi(r)$ via the expression 3.6. For any vector or scalar function f that tends to zero at infinity the following lemma is valid:

$$\text{if}\qquad g(r) = \nabla f(r), \qquad \text{then}\quad g^q(q) = iq\, f^q(q)$$

<div align="right">A2.3</div>

With the help of the relations A2.3 and of the Poisson equation (see expression 3.7) one can obtain:

$$\varphi^q(q) = 4\pi\frac{\rho^q(q)}{q^2}$$

<div align="right">A2.4</div>

For any two functions φ and ρ (let us take, as an example, the electrostatic field potential and the local electrostatic charge density) the following equation is valid:

$$\int d^3r\varphi(r)\rho(r) = \int\frac{d^3q}{(2\pi)^3}\ \varphi^q(q)\rho^q(-q)$$

<div align="right">A2.5</div>

Let us transform the expression 3.6 which describes the energy of electrostatic field in the system by means of first successively applying the expressions A2.5 and A2.4 and, second, substituting the expression A2.2. If the system is in the unperturbed state, i.e. there are no fluctuations of its components concentrations, there is no electrostatic field in it. Therefore, after these transformations one obtains the caused by electrostatic field increment $\delta F_{el\text{-}st}$ of the system's free energy in the perturbed state as compared to the unperturbed state:

$$\frac{\delta F_{el\text{-}st}a^3}{kT} = \frac{1}{2}\int\frac{d^3q}{(2\pi)^3}4\pi u\frac{\left(\delta\Phi_+^q(q) - \delta\Phi_-^q(q)\right)\left(\delta\Phi_+^q(-q) - \delta\Phi_-^q(-q)\right)}{q^2 a^2}$$

<div align="right">A2.6</div>

Entropic contribution to the system's free energy is expressed in the common way:

$$\frac{F_{tr\text{-}ent}}{kT} = \frac{1}{a^3}\int_V d^3r\left(\Phi_+(r)\ln\Phi_+(r) + \Phi_-(r)\ln\Phi_-(r) + \Phi_s(r)\ln\Phi_s(r)\right)$$

<div align="right">A2.7</div>

The difference of the entropic contribution $\delta F_{tr\text{-}ent}$ in the perturbed and in the unperturbed states is equal to:

$$\frac{\delta F_{tr\text{-}ent}(\delta\Phi_+,\delta\Phi_-)a^3}{kT} =$$

$$= \int_V d^3r \left\{ \frac{1}{\Phi}\left(\delta\Phi_+(r)^2 + \delta\Phi_-(r)^2\right) + \left(\delta\Phi_+(r) + \delta\Phi_-(r)\right)^2 \frac{1}{2(1-\Phi)} \right\} \qquad \text{A2.8}$$

For the derivation of the equation A2.8 expansion of the expression A2.7 into the Taylor series in terms of the small volume fraction fluctuations $\delta\Phi_+(r)$ and $\delta\Phi_-(r)$ has been done with using the expression 3.12. The expansion has been truncated after the second-order term. In addition, the terms linear in $\delta\Phi_+(r)$ and $\delta\Phi_-(r)$ have been excluded, because they produce contributions that are equal to zero, as it follows from the equation 4.3.

As compared to the unperturbed state, in the perturbed state of the system increment δF_{int} of its free energy related to contact interactions of the components molecules (see eq. A1.15) is exactly equal to:

$$\frac{\delta F_{int}(\delta\Phi_+,\delta\Phi_-)a^3}{kT} = \int_V d^3r \left[-\Delta\chi\left(\delta\Phi_+(r)^2 - \delta\Phi_-(r)^2\right) - \right.$$

$$- \chi\left(\delta\Phi_+(r) + \delta\Phi_-(r)\right)^2 + \chi_{+-}\delta\Phi_+(r)\delta\Phi_-(r) +$$

$$+ \frac{a^2}{6}\left[\chi\left(\nabla\delta\Phi_+(r) + \nabla\delta\Phi_-(r)\right)^2 + \right. \qquad \text{A2.9}$$

$$\left. + \Delta\chi\left(\left(\nabla\delta\Phi_+(r)\right)^2 - \left(\nabla\delta\Phi_-(r)\right)^2\right) - \chi_{+-}\nabla\delta\Phi_+(r)\nabla\delta\Phi_-(r) \right]$$

An IL/nIL homogeneous mixture free energy total increment δF caused by the appearing in it of the small components concentrations fluctuations is equal to the sum of the electrostatic and the entropic increments and of the increment caused by contact interactions of the components molecules. That is, it is equal to the sum of the expressions A2.6, A2.8, and A2.9:

$$\delta F = \delta F_{el-st} + \delta F_{tr-ent} + \delta F_{int} \qquad \text{A2.10}$$

Let us use again the equations A2.3 and A2.5 to express the contributions $\delta F_{tr\text{-}ent}$ and δF_{int} in the reciprocal Fourier coordinates. After that the sum A2.10 can be

calculated and the following expression of the total free energy increment δF in the reciprocal Fourier coordinates can be obtained:

$$\frac{\delta F(\delta\Phi_+,\delta\Phi_-)a^3}{kT}=$$

$$=\int\frac{d^3q}{(2\pi)^3}\left\{\frac{1}{\Phi}\left(\delta\Phi_+^q(q)\delta\Phi_+^q(-q)+\delta\Phi_-^q(q)\delta\Phi_-^q(q)\right)-\Delta\chi\left(\delta\Phi_+^q(q)\delta\Phi_+^q(-q)-\right.\right.$$

$$-\delta\Phi_-^q(q)\delta\Phi_-^q(-q)\right)+\left(\delta\Phi_+^q(q)+\delta\Phi_-^q(q)\right)\left(\delta\Phi_+^q(-q)+\delta\Phi_-^q(-q)\right)\left(\frac{1}{2(1-\Phi)}-\chi\right)+$$

$$+\chi_{+-}\delta\Phi_+^q(q)\delta\Phi_-^q(-q)+\frac{q^2a^2}{6}\left[\chi\left(\delta\Phi_+^q(q)+\delta\Phi_-^q(q)\right)\left(\delta\Phi_+^q(-q)+\delta\Phi_-^q(-q)\right)+\right.$$

$$+\Delta\chi\left(\delta\Phi_+^q(q)\delta\Phi_+^q(-q)-\delta\Phi_-^q(q)\delta\Phi_-^q(-q)\right)-\chi_{+-}\delta\Phi_+^q(q)\delta\Phi_-^q(-q)\right]+ \qquad \text{A2.11}$$

$$+2\pi u\frac{\left(\delta\Phi_+^q(q)-\delta\Phi_-^q(q)\right)\left(\delta\Phi_+^q(-q)-\delta\Phi_-^q(-q)\right)}{q^2a^2}\right\}$$

To obtain the value of the free energy increment corresponding to the fluctuation $\delta\Phi_+(r)$ of the cations volume fraction one needs to minimize the expression A2.11 over the fluctuation $\delta\Phi_-(r)$ of the anions volume fraction (of course, the cations and the anions could be interchanged in this statement). As a result, one obtains:

$$\delta F(\delta\Phi_+)=\int\frac{dq}{(2\pi)^3}\delta\Phi_+^q(q)\delta\Phi_+^q(-q)G\left(\chi,\Delta\chi,\chi_{+-},u,\Phi,q\right)+const \qquad \text{A2.12}$$

About the technique of this minimization one can read, for example, in the work [85]. The value G depends on the parameters χ, $\Delta\chi$, χ_{+-}, u, Φ, and on the modulus q of the wave vector. The final expression which describes the value G is presented in the chapter 4 (see eq. 4.6) where it is used later on.

If the cations volume fraction fluctuation is a harmonic one:

$$\delta\Phi_+(r)=A_+\cos(q_0 r) \qquad \text{A2.13}$$

then its Fourier transform is expressed as:

$$\delta\Phi_+^q(q)=\frac{1}{2}(2\pi)^3 A_+\left[\delta(q-q_0)+\delta(q+q_0)\right] \qquad \text{A2.14}$$

The corresponding to this fluctuation mixture's free energy increment can be obtained by means of substituting the expression A2.14 into the expression A2.12. As a result, the expression 4.5 can be obtained.

Now let us consider a small concentrations fluctuation in a pure IL. In this case, fluctuations of the cations and the anions volume fractions are not independent, but they are connected via the equality $\delta\Phi_+(r) + \delta\Phi_-(r) = 0$ because the IL is supposed to be incompressible. Besides, in this case, the volume fraction of IL is equal to unity in all points of the system. With taking this into account, one can obtain the expression of the free energy increment δF caused by the fluctuation $\delta\Phi_+(r)$ as a special case of the expression A2.11 after excluding from it all the terms connected with the nonionic solvent:

$$\frac{\delta F(\delta\Phi_+)a^3}{kT} = \int \frac{d^3q}{(2\pi)^3} \delta\Phi_+(q)\delta\Phi_+(-q)\left[2 - \chi_{+-} + \chi_{+-}\frac{q^2a^2}{6} + \frac{8\pi u}{q^2a^2}\right] \qquad \text{A2.15}$$

where the square brackets comprise nothing else but the expression of the variable G for the considered case (see the equation 4.15).

References.

1. Sheldon R. Catalytic reactions in ionic liquids. // Chem. Commun. 2001. I. 23. pp. 2399 – 2407.

2. Wasserscheid P., Welton T. Ionic Liquids in Synthesis. – Wiley-VCH: New York. 2002.

3. Dupont J., Souza R.F., Suarez P.A.Z. Ionic Liquid (Molten Salt) Phase Organometallic Catalysis. // Chem. Rev. 2002. V. 102. pp. 3667 – 3692.

4. Abbott A.P., Capper G., Davies D.L., Munro H.L., Rasheed R.K., Tambyrajah V. Preparation of novel, moisture-stable, Lewis-acidic ionic liquids containing quaternary ammonium salts with functional side chains. // Chem. Commun. 2001. I. 19. pp. 2010 – 2011.

5. Dupont J. // On the Solid, Liquid and Structural Organization of Imidazolium Ionic Liquids. J. Braz. Chem. Soc. 2004. V. 15. pp.341-350.

6. Greaves T.L., Drummond C.J. Protic Ionic Liquids: Properties and Applications. // Chem. Rev. 2008. V. 108. pp. 206 – 237.

7. MacFarlane D.R., Seddon K.R. Ionic Liquids – Progress on the Fundamental Issues. // Aust. J. Chem. 2007. V. 60. pp. 3 – 5.

8. Welton T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. // Chem. Rev. 1999. V. 99. pp. 2071 – 2084.

9. Earle M.J., Esperança J.M.S.S., Gilea M.A., Canongia Lopes J.N., Rebelo L.P.N., Magee J.W., Seddon K.R., Widegren J.A. The distillation and volatility of ionic liquids. // Nature. 2006. V. 439. pp. 831 – 834.

10. Holbrey J.D., Seddon K.R. Ionic liquids. // Clean Products and Processes. 1999. V. 1. pp. 223-236.

11. Zhao H. Innovative Applications of Ionic Liquids as "Green" Engineering Liquids. // Chem. Eng. Comm. 2006. V. 193. pp. 1660-1677

12. Swatloski R.P., Spear S.K., Holbrey J.D., Rogers R.D. Dissolution of Cellose with Ionic Liquids. // J. Am. Chem. Soc. 2002. V. 124. pp. 4974 – 4975.

13. Armstrong D. W., L. He, Liu Y.-S. Examination of Ionic Liquids and Their Interaction with Molecules, When Used as Stationary Phases in Gas Chromatography. // Anal. Chem. 1999. V. 71. pp. 3873-3876.

14. Anderson J.L., Armstrong D.W. High-Stability Ionic Liquids. A New Class of Stationary Phases for Gas Chromatography. // Anal. Chem. 2003. V. 75. pp. 4851-4858.

15. Ding J., Welton T., Armstrong D.W. Chiral Ionic Liquids as Stationary Phases in Gas Chromatography. // Anal. Chem. 2004. V. 76. pp. 6819 – 6822.

16. Aerov A.A., Khokhlov A.R., Potemkin I.I. Why Ionic Liquids Can Possess Extra Solvent Power. // J. Phys. Chem. B. 2006. V.110. pp. 16205 –16207.

17. Barhdadi R., Courtinard C., Nédélec J.Y., Troupel M. Room-temperature ionic liquids as new solvents for organic electrosynthesis. The first examples of direct or nickel-catalysed electroreductive coupling involving organic halides. // Chem. Commun. 2003. I. 12. pp. 1434 – 1435.

18. Canongia Lopes J.N., Cordeiro T.C., Esperanca J.M.S.S., Guedes H.J.R., Huq S., Rebelo L.P.N., Seddon K.R. Deviations from Ideality in Mixtures of Two Ionic Liquids Containing a Common Ion. // J. Phys. Chem. B. 2005. V. 109. pp. 3519 – 3525.

19. Aerov A.A., Khokhlov A.R., Potemkin I.I. Interface between Ionic and Nonionic Liquids: Theoretical Study. // J. Phys. Chem. B. 2007. V. 111. pp. 3462 – 3468.

20. Aerov A.A., Khokhlov A.R., Potemkin I.I. Microphase Separation in a Mixture of Ionic and Nonionic Liquids. // J. Phys. Chem. B. 2007. V. 111. pp. 10189 – 10193.

21. Riisager A., Fehrmann R., Haumann M., Gorle B.S.K., Wasserscheid P. Stability and Kinetic Studies of Supported Ionic Liquid Phase Catalysts for Hydroformylation of Propene. // Ind. Eng. Chem. Res. 2005. V. 44. pp. 9853 – – 9859.

22. Frackowiak E., Lota G., Pernak J. Room-temperature phosphonium ionic liquids for supercapacitor application. // Applied physics letters. 2005. V. 86. pp. 164104-1 – 164104-3.

23. Wang P., Zakeeruddin S.M., Comte P., Exnar I., Grätzel M. Gelation of Ionic Liquid-Based Electrolytes with Silica Nanoparticles for Quasi-Solid-State Dye-Sensitized Solar Cells. // J. Am. Chem. Soc. 2003. V.125. pp. 1166 – 1167.

24. Audic N., Clavier H., Mauduit M., Guillemin J.C. An Ionic Liquid-Supported Ruthenium Carbene Complex: A Robust and Recyclable Catalyst for Ring-Closing Olefin Metathesis in Ionic Liquids. // J. Am. Chem. Soc. 2003. V. 125. pp. 9248 – 9249.

25. Bowers J., Vergara-Gutierrez M.C., Webster J.R.P. Surface Ordering of Amphiphilic Ionic Liquids. // Langmuir. 2004. V. 20. pp. 309 – 312.

26. Najdanovic-Visak V., Esperanca J.M.S.S., Rebelo L.P.N., Ponte M.N., Guedes H.J.R., Seddon K.R., Sousa H.C., Szydlowski J. Pressure, Isotope, and Water Co-solvent Effects in Liquid-Liquid Equilibria of (Ionic Liquid + Alcohol) Systems. // J. Phys. Chem. B. 2003. V. 107. pp. 12797 – 12807.

27. Crosthwaite J.M., Aki S.N.V.K., Maginn E.J., Brennecke J.F. Liquid Phase Behavior of Imidazolium-Based Ionic Liquids with Alcohols. // J. Phys. Chem. B. 2004. V. 108. pp. 5113 – 5119.

28. Lachwa J., Szydlowski J., Najdanovic-Visak V., Rebelo L.P.N., Seddon K.R., Ponte M.N.,. Esperanca J.M.S.S, Guedes H.J.R. Evidence for Lower Critical Solution Behavior in Ionic Liquid Solutions. // J. Am. Chem. Soc. 2005. V. 127. pp. 6542 – 6543.

29. Najdanovic-Visak V., Esperanca J.M.S.S, Rebelo L.P.N., Ponte M.N., Guedes H.J.R., Seddon K.R., Szydlowskiy J. Phase behavior of room temperature ionic liquid solutions: an unusually large co-solvent effect in (water + ethanol). // Phys. Chem. Chem. Phys. 2002. V. 4. pp. 1701 – 1703.

30. Dekker C. Carbon Nanotubes as Molecular Quantum Wires. // Physics Today. 1999 V. 52, pp. 22 – 28.

31. Fukushima T., Kosaka A., Yamamoto Y., Aimiya T., Notazawa S., Tagikawa T., Inabe T., Aida T. Dramatic effect of Dispersed Carbon Nanotubes on the Mechanical and Electroconductive Properties of Polymers Derived from Ionic Liquids // Small. 2006. V. 2. pp. 554-560.

32. Fukushima T., Kosaka A., Ishimura Y., Yamamoto T., Tagikawa T., Ishii N., Aida T. Molecular Ordering of Oranic Molten Salts Triggered by Single-Walled Carbon Nanotubes. // Science. 2003. V. 300. pp. 2072 – 2074.

33. Tang J., Sun W., Tang H., Radosz M., Shen Y. Enhanced CO_2 Absorption of Poly(ionic liquid)s. // Macromolecules. 2005. V. 38. pp. 2037 – 2039.

34. Bates E.D., Mayton R.D., Ntai I., Davis J.H. CO_2 Capture by a Task-Specific Ionic Liquid. // J. Am. Chem. Soc. 2002. V. 124. pp. 926 -927.

35. Fukushima T., Asaka K., Kosaka A., Aida T. Fully Plastic Actuator through Layer-by-Layer Casting with Ionic-Liquid-Based Bucky Gel. // Angew. Chem. Int. Ed. 2005. V. 44. pp. 2410-2413.

36. Weiss V.C., Schröer W. The liquid-vapour interface of the restricted primitive model (RPM) of ionic fluids. // J. Phys.: Condens. Matter. 2000. V.12. pp. 2637 – 2655.

37. Valleau J.P. The Coulombic phase transition: Density-scaling Monte Carlo. // J. Chem. Phys. 1991. V. 95. pp. 584 – 589.

38. Caillol J.M. A Monte Carlo study of the liquid–vapor coexistence of charged hard spheres. // J. Chem. Phys. 1994. V. 100. pp. 2161 – 2169.

39. Guillot B., Guissani Y. Towards a theory of coexistence and criticality in real molten salts. // Molecular physics. 1996. V. 87. pp. 37 – 86.

40. Fisher M.E. The Story of Coulombic Criticality // Journal of Statistical Physics. 1994. V. pp. 1 – 36.

41. Stell G. Criticality and Phase Transitions in Ionic Fluids. // J. Stat. Phys.1995. V. 78. pp. 197 – 238.

42. Singh R.R., Pitzer K.S. Near-critical coexistence curve and critical exponent of an ionic fluid. // J. Chem. Phys. 1990. V. 92. pp. 6775 – 6778.

43. Zhang K.C., Briggs M.E., Gammon R.W. The susceptibility critical exponent for a nonaqueous ionic binary mixture near a consolute point. // J. Chem. Phys. 1992. V. 97. pp. 8692 – 8697.

44. Japas M.L., Levelt Sengers J.M.H. Critical behavior of a conducting ionic solution near its consolute point // J. Phys. Chem. 1990. V. 94. pp. 5361 – 5368.

45. Fisher M.E., Levin Y. Criticality in ionic fluids: Debye-Hückel theory, Bjerrum, and beyond. // Phys. Rev. Lett. 1993. V.71. pp. 3826 – 3829.

46. Orkoulas G., Panagiotopoulos Z. Free energy and phase equilibria for the restricted primitive model of ionic fluids from Monte Carlo simulations. // J. Chem. Phys. 1994. V. 101. pp. 1452 – 1459.

47. Caillol J.M. A new potential for the numerical simulations of electrolyte solutions on a hypersphere. // J. Chem. Phys. 1993. V. 99. pp. 8953 – 8963.

48. Panagiotopoulos Z. Molecular simulation of phase equilibria: simple, ionic and polymeric fluids. // Fluid Phase Equilibria. 1992. V. 76. pp. 97 – 112.

49. Friedman H.L. Corresponding states for ionic fluids. // J. Chem. Phys. 1979. V. 70. pp. 92 – 100.

50. Weiss V.C., Schröer W. Macroscopic theory for equilibrium properties of ionic-dipolar mixtures and application to an ionic model fluid. // J. Chem. Phys. 1998. V. 108. pp. 7747 – 7757.

51. Orkoulas G., Panagiotopoulos Z. Phase behavior of the restricted primitive model and square-well fluids from Monte Carlo simulations in the grand canonical ensemble. // J. Chem. Phys. 1999. V. 110. pp. 1581 – 1590.

52. Caillol J. M., Levesque D., Weis J.J. A Monte Carlo finite size scaling study of charged hard-sphere criticality // J. Chem. Phys. 1997. V. 107. pp. 1565 – 1575.

53. Onuki A. Ginzburg-Landau theory of solvation in polar fluids: Ion distribution around an interface. // Phys. Rev. E. 2006. V. 73. pp. 021506-1 –021506-16.

54. Kitamura H., Onuki A. Ion-induced nucleation in polar one-component fluids. // J. Chem. Phys. 2005. V.123. pp. 124513-1 – 124513-9.

55. Onuki A., Kitamura H. Solvation effects in near-critical binary mixtures. // J. Chem. Phys. 2004. V. 121. pp. 3143 – 3151.

56. Onuki A. Liquid Crystals in Electric Field. // Journal of the Physical Society of Japan. 2004.V. 73. pp. 511 – 514.

57. Levin Y., Flores-Mena J.E. Surface tension of strong electrolytes. // Europhys. Lett. 2001. V. 56. pp. 187 – 192.

58. Matubayasi N., Matsuo H., Yamamoto K., Yamaguchi S., Matuzawa A. Thermodynamic Quantities of Surface Formation of Aqueous Electrolyte Solutions: Aqueous Solutions of NaCl, $MgCl_2$, and $LaCl_3$. // Journal of Colloid and Interface Science. 1999. V. 209. pp. 398 – 402.

59. Hsin W.L., Sheng Y.J., Lin S.Y., Tsao H.K. Surface tension increment due to solute addition. // Phys. Rew. E. 2004. V. 69. pp. 031605-1 – 031605-8.

60. Onsager L., Samaras N.T. The Surface Tension of Debye-Hückel Electrolytes. // J. Chem. Phys. 1934. V. 2. pp. 528 – 536.

61. Ohshima H. Surface tension of general electrolyte solutions. // Colloid Polym. Sci. 2004. V. 283. pp. 119 – 124.

62. Vasilevskaya V.V., Aerov A.A., Khokhlov A.R. ''Swiss-cheese'' polyelectrolyte gels as media with extremely inhomogeneous distribution of charged species. // J. Chem. Phys. 2004. V.120. pp. 9321 – 9329.

63. Boström M., Williams D.R.M., Ninham B.W. Surface Tension of Electrolytes: Specific Ion Effects Explained by Dispersion Forces. // Langmuir. 2001. V. 17. pp. 4475 – 4478.

64. Ho C.H., Tsao H.K. Interfacial tension of a salty droplet: Monte Carlo study. // J. Chem. Phys. 2003. V. 119. pp. 2369 – 2375.

65. Gonza´lez-Melchor M., Alejandre J., Bresme F. Surface Tension of the Restrictive Primitive Model for Ionic Liquids. // Phys. Rev. Lett. 2003. V. 90. pp. 135506-1 – 135506-4.

66. Rebelo L.P.N., Najdanovic-Visak V., Visak Z.P., Ponte M. N., Szydlowski J., Cerdeiriña C.A., Troncoso J., Romaní L., Esperança M.S.S., Guedesc H.J. R., Sousa H.C. A detailed thermodynamic analysis of [C4mim][BF4] + water as a case study to model ionic liquid aqueous solutions. // Green Chem. 2004. V. 6. pp. 369 – 381.

67. Fan F.C., Olafson B.D., Blanco M. Application of Molecular Simulation To Phase Diagrams of Binary Mixtures // Macromolecules. 1992. V. 25. pp. 3667 – 3676.

68. Khokhlov A.R, Kuchanov S.I. Lectures on physical chemistry of polymers. – Moscow.: Mir. 2000. pp. 68 – 75.

69. Ishimatsu R., Shigematsu F., Hakuto T., Nishi N., Kakiuchi T. Structure of the Electrical Double Layer on the Aqueous Solution Side of the Polarized Interface between Water and a Room-Temperature Ionic Liquid, Tetrahexylammonium Bis(trifluoromethylsulfonyl)imide. // Langmuir. 2007. V. 23. pp. 925 – 929.

70. Canongia Lopes J.N.A., Padua A.A.H. Nanostructural Organization in Ionic Liquids. // J. Phys. Chem. B. 2006. V. 110. pp. 3330 – 3335.

71. Canongia Lopes J. N., Costa Gomes M.F., Padua A.A.H. Nonpolar, Polar, and Associating Solutes in Ionic Liquids. // J. Phys. Chem. B. 2006. V. 110. pp. 16816 – 16818.

72. Lachwa J., Bento I., Duarte M.T., Canongia Lopes J.N., Rebelo L.P.N. // Condensed phase behaviour of ionic liquid–benzene mixtures: congruent

melting of a [emim][NTf$_2$]·C$_6$H$_6$ inclusion crystal. // Chem. Commun. 2006. I. 23. pp. 2445 – 2447.

73. Deetlefs M., Hardacre C., Nieuwenhuyzen M., Sheppard O., Soper A.K. Structure of Ionic Liquid-Benzene Mixtures. // J. Phys. Chem. B. 2005. V. 109. pp. 1593-1598.

74. Potemkin I.I., Vasilevskaya V.V., Khokhlov A.R. Associating polyelectrolytes: Finite size cluster stabilization versus physical gel formation. // J. Chem. Phys. 1999. V. 111. pp. 2809 – 2817.

75. Limberger R.E., Potemkin I.I., Khokhlov A.R. Microphase separation in solutions of associating polyelectrolytes: Strong segregation approximation. // J. Chem. Phys. 2003. V. 119. pp. 12023 – 12028.

76. Blesic M., Marques M.H., Plechkova N.V., Seddon K.R., Rebelo L.P.N., Lopes A. Self-aggregation of ionic liquids: micelle formation in aqueous solution. // Green Chem. 2007. V. 9. pp. 481 – 490.

77. Vasilevskaya V.V., Aerov A.A., Khokhlov A.R. Control of reactions between surfactant reagents in miniemulsions. Surface nanoreactors. // Colloid Polym. Sci. 2005. V. 284. pp. 459 – 457.

78. Vasilevskaya V.V., Aerov A.A., Khokhlov A.R. Catalytic Reactions of a Surface-Active Catalyst and a Surface-Active Substrate in Emulsions: The Optimal Drop Size. // Doklady Physical Chemistry. 2004. V. 398. pp. 258 – 261.

79. Leibler L. Theory of Microphase Separation in Block Copolymers. // Macromolecules. 1980. V. 13. pp. 1602 – 1617.

80. Dormidontova E.E., Erukhimovich I.Ya., Khokhlov A.R. Microphase separation in poor-solvent polyelectrolyte solutions: phase diagram. // Macromol. Theor. Simul. 1994. V. 3. pp. 661 – 674.

81. Palyulin V.V., Potemkin I.I. Microphase Separation in Melts of Double Comb Copolymers. // Polym. Sci. A (Russia). 2007. V. 49. pp. 473-482.

82. Hornreich R.M., Luban M., Shtrikman S. Critical Behavior at the Onset of $k\rightarrow$-Space Instability on the λ Line. // Phys. Rev. Lett. 1975. V. 35. pp. 1678 – 1681.

83. Grosberg A.Yu., Khokhlov A.R. Statistical Physycs of Macromolecules. – AIP Press: New York. 1994.

84. Safran S.A. Statistical Thermodynamics of Surfaces, Interfaces, and Membranes. – Addison-Wesley Publishing Company. 1994. pp. 63 – 66.

85. Potemkin I.I., Limberger R.E., Kudlay A.N., Khokhlov A.R. Rodlike polyelectrolyte solutions: Effect of the many-body Coulomb attraction of similarly charged molecules favoring weak nematic ordering at very small polymer concentrations. // Physical Review E. 2002. V. 66. pp. 011802-1 – – 011802-11.

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Marital status:	single
Business address:	Chair of Polymer and Crystals Physics, Physics Department, Moscow State University
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PROFESSIONAL SKILLS

Languages:	Russian (native), English (fluently), Deutsch
Scientific skills:	Theory of polymer gels;
	Theory of emulsion catalysis;
	Random phase approximation technique;
	Theory of phase equilibrium in ion containing systems;
	Theory of phase boundaries.

EDUCATION and RESEARCH EXPERIENCE

2008-present	**Moscow, Russia**
	• Chair of Polymer and Crystals Physics, Physics Department, Moscow State University
	"*Swelling of a Microgel with immobilized Carbon Nanotubes in an Ionic Liquid: theoretical study.*"
	PhD student
2005-2008	**Moscow, Russia / Ulm, Germany**
	• Chair of Polymer and Crystals Physics, Physics Department, Moscow State University, and Department of Polymer Science, University of Ulm
	"*Theoretical study of Phase Equilibrium in binary mixtures comprising an Ionic Liquid.*"
	PhD student

1999-2005 **Moscow, Russia**
- **Physics Department, Moscow State University**
"Utilization of different physically microheterogenous systems for creation of controllable nanoreactors: theoretical study."
- **Master's Degree in Physics with the Specialization "Physics of Polymers."**

GRANTS

2005 **Scholarship of the government of the city of Moscow for Phd Students**
The laureate of the program "Grants of Moscow for science and education"

09/2008-11/2008 **DAAD scholarship under the "Ostpartnerschaften" program**

AWARDS

09/2006-09/2007 President of Russian Rederation Scholarship for Phd Students

2006 LG Chem Scholarship for Phd Students

2004 LG Chem Scholarship for Students

04/2008 Diploma for the report on the International conference of students, PhD students and young scientists. "Lomonosov-2008"

Ulm, 22.09.2008

Artem Aerov