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Ionic Liquid Surfactants

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Abstract—For the first time an overview of the available latest publications from the scientific and technical literature on surfactant ionic liquids is compiled. The methods of preparation, structural features, the most important physicochemical properties, and the areas of application of these substances are considered. Particular attention is paid to the data related to the properties of ionic liquids manifested at the interfaces. Applied properties of ionic liquid surfactants are demonstrated.

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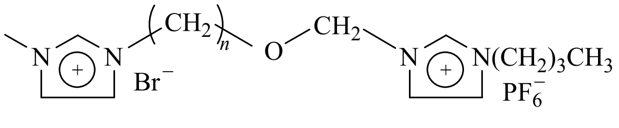
Ionic liquids consisting of a large-sized organic cation (mostly the nitrogen-containing one) and a considerably smaller inorganic anion are compounds with a melting point below 150°C. Various combinations of cations and anions are described capable to form ionic liquids [1–5].

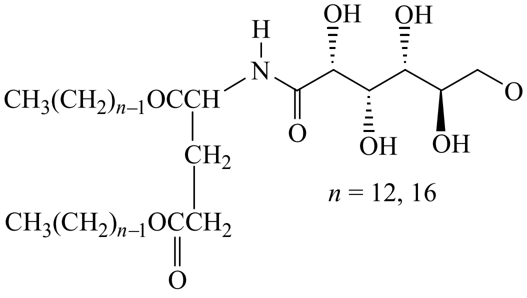
Variety of properties of ionic liquids, including the ability to dissolve a large number of inorganic and organic, including polymeric substances, their non-corrosive properties, low viscosity, and insignificant vapor pressure attract an increasing interest to their use in multiphase homogenous catalytic reactions [6–11], when one phase chosen to dissolve a catalyst does not mix with another phase, which contains the initial and final products. Similar catalysis, as expected, occurs at the boundary of the ionic liquids and the upper organic phase. A clearer understanding of the mechanisms of these catalytic processes requires the knowledge of surface properties of the ionic liquids. For this reason, the data concerning the surface activity of ionic liquids, including the literature data on surface active ionic liquids, are considered in the present article separately.

An European patent [12] discloses a new class of ionic liquids and methods of their preparation. These ionic liquids can be obtained on the basis of such anionic surfactants as alkylarylsulfonates and alkyl sulfate, alkylalkoxysulfonate and alkylarylsulfate derivatives branched in the middle of the chain. Similar ionic liquids can be produced also from the sulfonates like alkyl glycerol ethers, methyl sulfonates, and sulfonates of α-olefins. The anions are combined with various cations supplying the final product with a variety of useful, including surfactant, properties.

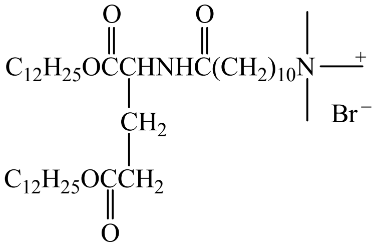
Kimizuka et al. [13] synthesized a series of surface-active ionic liquid substances composed of fragments of ethers and esters:

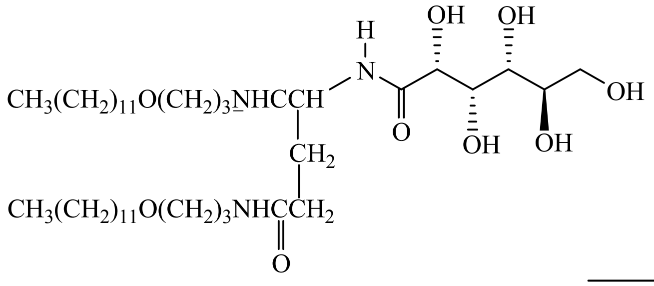


$n = 1, 2$



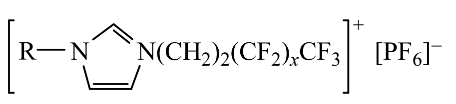
$n = 12, 16$





These ionic liquids are capable of dissolving carbohydrates like D-glucose, cyclodextrin, amylose, agarose, glucoprotein, oxidized glucose. When glycollipides are dispersed in an ionic liquid having affinity to carbohydrates, a stable double-layer membrane is formed. In such membranes a reversible thermal transformation was observed that includes the structures in the range from fibrillary aggregates to vesicles. Physical gelation of ionic liquids is due to the dissolution of glycolipids enriched with lipid groups. The authors marked that the mentioned properties of the self-forming gels (capability of dissolving carbohydrates, forming two-layer membrane) provide the opportunity for the development of new directions in research of ionic liquids. Unfortunately, the paper does not provide specific data on the surface properties of the synthesized compounds.

Merrigan et al. [14, 15] report on the synthesis of imidazolium ion with a long "tail" chain, which forms a part of the low-melting fluoride ionic liquids. The formation of a liquid-crystalline phase was observed, and it was therefore suggested that the association of fluorocarbon chains occurred in these ionic liquid cations. In [14] the synthesis was described of four new fluorinated ionic liquids that were significantly different from the known fluoride ionic liquids [16–19] by the presence of a long fluorinated alkyl chain in the cation part.



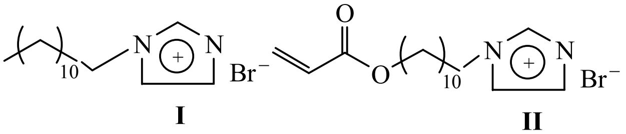
R = CH_3, x = 5 (**a**); R = n-C_4H_9, x = 5 (**b**); R = CH_3, x = 7 (**c**); R = n-C_4H_9, x = 7 (**d**).

Melting points of these salts are 61, 88, 87, and 97°C respectively, the temperature of appearance of transparency 109, 134, 130, and 145°C, respectively.

All four salts are surfactants and promote formation and stabilization of perfluorinated hydrocarbon dispersions in the medium of a common ionic liquids [hmim]·[PF_6] (1-hexyl-3-methylilmidazolium hexafluorophosphate). To obtain these fluorinated ionic liquids [14] imidazole derivatives, namely 1-methyl- and 1-butylimidazole were dissolved in toluene, treated with a small molar deficit of 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodooctane or 1,1,1,2,2,3,3,4,4,5,5,6,6,·7,7,8,8-heptadecafluoro-10-iodododecane, and the mixture was heated. After cooling to room temperature followed by removal of the solvent in a vacuum, a gray-white substance was obtained. These iodide salts readily undergo metathesis with $AgPF_6$ in acetone to form the ionic liquids in good yields. These compounds show a number of the surfactant properties. Measurements by the method of the capillary rise of level showed that the surface tension of the saturated solution (0.3 wt %, namely, ~1–4 millimolar solution) in [hmim][PF_6] was by 10–15% less than with the ionic liquid proper. The viscometric measurements showed that, as in the case of conventional surfactants [20], the addition of these fluorine-containing surfactant ionic liquids to [hmim][PF_6] increased the viscosity of the latter. But the most surprising feature of these fluorinated surfactant ionic liquids is their ability to form and stabilize the perfluorohexane dispersions in usual ionic liquids, namely, in [hmim][PF_6].

In [21] a quaternization reaction was used with microwave radiation for the synthesis of a series of ionic liquid salts, which include triethylhexylammonium bromide, triethyldodecylammonium bromide, triethyloctadecylammonium bromide, 1-methyl-3-tetradecylimidazolium bromide, 1-methyl-3-octadecylimidazolium bromide, 1-tetradecylpiridinium bromide, 1-octadecylpiridinium bromide, tripentylmethylammonium chloride, trihexylmethylammonium chloride, and trioctylmethylammonium chloride. These salts were identified using the ^{1}H and ^{13}C NMR spectroscopy. All these ionic liquids at concentration 1000 ppm and 80°C show good demulsifying capacity towards the typical crude oil. The demulsifying capacity of each of the salts decreases with increasing density of the oil. The important role of the alkyl group at demulsification was demonstrated. Best results were obtained when the chain contained 12 or 14 carbon atoms.

Synthesis of the surface-active ionic liquids consisting of imidazolium cation and a hydrophobic chain was reported [22].


I **II**

They are used to stabilize the microemulsion. The first ionic liquid surfactant [C_{12}-mim]Br (**I**) was synthesized by the reaction of 1-bromdodecanol with 1-methylimidazole. In the synthesis of 1-(2-acryloyloxyundecyl)-3-methylimidazolium bromide (**II**), initially the acryloyl chloride reacted with 11-bromoundecanol-1 in equimolar amounts in tetrahydrofuran to obtain bromoalkyl acrylate. In a reaction with 1-methylimidazole this compound forms bromide **II**, which is capable to polymerize. Both products are ionic liquids at room temperature.

The critical micelle-formation concentration of bromide **I** in water determined by the measurement of the surface tension by the drop method is 10.31 mM at 34°C. The microemulsion polymerization in the α-Br-methyl metacrylate–H_2O system (weight ratio of 0.04:0.04:0.92) was initiated with azobisisobutyronitrile at 60°C. During polymerization turbidity occurred due to the aggregation of the particles. The resulting polymer latexes are monodisperse, with the particle diameter about 50 nm.

The critical micelle-formation concentration of bromide **II** found by the above method is 15.35 mM at 24°C. Like the non-polymerizing bromide **I**, bromide **II** can be used for the stabilization of the H_2O–methylmetacrylate system to form a transparent and stable microemulsion. The observed benefit of the polymerizable surfactants in comparison with non-polymerizing one is that it allows to obtain microemulsions of nanoscale and nanostructure as a result of polymerization [22]. The polymerization of the microemulsion system of **II**–methyl metacrylate–H_2O (weight ratio 0.07:0.07:0.86) leads to a polymer latex with no apparent aggregation. The copolymerization of methyl metacrylate with ionic liquids surfactant **II** to form the microemulsion was confirmed by the FTIR spectroscopy. The average diameter of the nanoparticle is ~30 nm as determined by the method of transmission electron microscopy. Since bromide **II** is more polar than methyl metacrylate, it likely forms a polymerizable polar shell around the formed particles, which increases the stability of the particles and allows easy redispersing of the particles in water and NaBr solution without noticeable aggregation. This indicates that the surface of the latex is a hydrophilic one. These latexes begin to aggregate in $NaBF_4$. A strong aggregation occurs in KPF_6 solution. This aggregation is caused by the conversion of the hydrophilic surface into hydrophobic when the anion Br^- is replaced by BF_4^- or PF_6^- [23, 24].

Zhang et al. [25] synthesized a series of new surface-active ionic liquids based on *N*-methyl-2-pyrrolidone and alkyl bromide. The physical properties of these salts were described: they have the characteristics of ionic liquids, the surface activity and biocompatibility. In view of this circumstance the authors classified these salts as the “green” ionic liquids.

In [26] a new modular architecture of surfactants was developed based on compounds related to RTIL (room temperature ionic liquids). These surfactants can be transformed to either polymerizable, or non-polymerizable form, therewith the molecules form a phase of lyotropic liquid crystal with a dual continuity. These phases include three-dimensional interconnected periodic nanopores when mixed with water or other RTIL as a solvent. The polymerizable analogs of these surfactants can be transformed into a stable nanopore organic materials by *in situ* cross-linking (polymerization of the monomers in water and lyotropic liquid-crystalline phases based on RTIL). This technology allows to obtain a set of polymer nanomaterials based on the RTIL with superior accessibility of pores and the properties of molecular transport (or exclusion according to size) in comparison with the known liquid-crystalline and polymer RTIL materials. The high accessibility of pores of these materials and selectivity with respect to the molecular size in the cubic structure with double continuity in combination with the chemical properties of water or RTIL in channels makes it possible to achieve high performance in several applications (nanofiltration, gas separation, materials with barrier to vapor, the ionic conductivity, preventing pollution and damage of proteins, electrochemistry, catalysis).

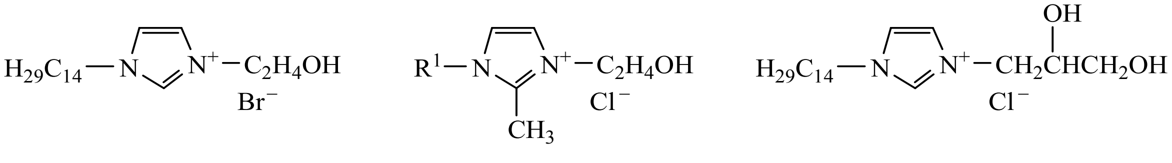
The catanionic (cation-anionic) surfactants comprise a special class of surfactants, in which both ions are organic. If the hydrophobic hydrocarbon chains of the two organic ions have the same length (strictly speaking, two organic ions should have the same surface activity), the catanionic surfactant is classified as symmetric [27]. In aqueous solution both the surface-active ions roll up. In the micelles and the adsorption layer they are in approximately equal amounts, that is, the mole fraction of each ion is equal to 0.5 [28]. Eventually, the surface tension $-\sigma_0$ (before adsorption) is changed to σ (after adsorption).

According to the model of mass action, or model of the division of the charged pseudophase [28], a change in the standard free energy of micelle formation (ΔG_M) of a symmetric catanionic surfactant is described by the equation $\Delta G_\mathrm{M} = 2RT \ln c_\mathrm{CMC}$.

The analysis of changes in the free energy transfer at the micelle formation (ΔG_M) and surface adsorption (ΔG_A) of the catanionic surfactants resulted in two important conclusions: (1) The values of $\Delta G_\mathrm{M}^0(\mathrm{CH_2})$ calculated from either the mass action (or division of the charged phases) model or the model of the free energy of the hydrocarbon/water interface are in good agreement with each other (~ -3 kJ mol^{-1}) [29], the same is true for $\Delta G_\mathrm{A}^0(\mathrm{CH_2})$. (2) From the values of ΔG_M^0 (or ΔG_A^0) and $\Delta G_\mathrm{M}^0(\mathrm{HC})$ [or $\Delta G_\mathrm{A}^0(\mathrm{HC})$] [$\Delta G_\mathrm{M}^0$ can be divided into $\Delta G_\mathrm{M}^0(\mathrm{HC})$ and $\Delta G_\mathrm{M}^0(\mathrm{W})$ for the hydrocarbon chain and hydrophilic *head*, respectively] fairly constant values of $\Delta G_\mathrm{M}^0(\mathrm{W})$ and $\Delta G_\mathrm{A}^0(\mathrm{W})$ can be obtained for homological catanionic surfactants. The spontaneous folding of the surfactants hydrocarbon chain in aqueous solution was also confirmed. If the hydrocarbon chain were in a fully extended conformation in aqueous solution, the value of molecular area of the hydrocarbon chain of surfactant in contact with water would be much larger than for the spontaneously folded conformation, and the value of $\Delta G_\mathrm{M}^0(\mathrm{CH_2})$ or $\Delta G_\mathrm{A}^0(\mathrm{CH_2})$ would be equal not to -3 kJ mol^{-1}, but to about -6.5 kJ mol^{-1}, which is obviously impossible, showing that the extended conformation of the hydrocarbon chain does not exist.

It is noteworthy that the value of $\Delta G_\mathrm{A}^0(\mathrm{W})$ is much larger than $\Delta G_\mathrm{M}^0(\mathrm{W})$. This may be due to a very dense packing and, therefore, much greater dehydration of the ionic *head* on the surface of the solution during adsorption. For example, for $\mathrm{C_8NM^+{-}C_8S^-}$ ($\mathrm{NM^+}$ is trimethylammonium cation, and $\mathrm{S^-}$ is sulfate anion) the average surface-molecular area of the orientation hydrophobic chain is 29 Å^2, while the average area occupied by surfactant molecules on the surface of the micelle equals ~69 Å^2.

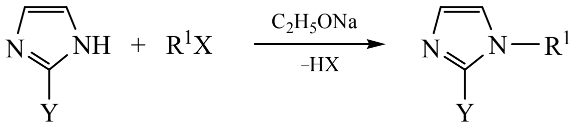
Aqueous solutions of $\mathrm{C}_n\mathrm{NM^+{-}C}_n\mathrm{S^-}$, where n = 8, 10, and 12, become turbid after reaching critical micelle-formation concentration, and phase separation occurs [30]. It was suggested that it was not a true critical micelle-formation concentration but the solubility limit, as the micelles are so large that they form a new concentration of phase of the surfactants. However, the results are interesting and show that in this case the critical micelle-formation concentration is real and that the micelles are of the spherical shape, at least at the critical micelle-formation concentration. The fact that $\mathrm{C_8NE^+{-}C}_n\mathrm{S^-}$, where $\mathrm{NE^+}$ is triethylammonium cation, can form a clear micellar solution and its standard free energy is similar to that of $\mathrm{C}_n\mathrm{NM^+{-}C}_n\mathrm{S^-}$, can be considered as a parallel evidence of this statement.



$\mathrm{R^1 = C_{12}H_{25}, C_{14}H_{29}, C_{16}H_{33}}$.

Dorjnamjin et al. [31] synthesized a series of cationic imidazolium ionic liquids of the surfactant nature (the formulas are shown above) for the use as reducers of silver and the protector of the formed nanoparticles of the metal. For the synthesis a quaternization was used with 1-chloroethanol and 1-chloropropane-2,3-diol.

For the prior introduction of a long alkyl substituent in the imidazole ring an exchange reaction was carried out.



Y = H, $\mathrm{CH_3}$; X – halogen.

It is shown that ionic liquids form complexes with silver particles, thereby stabilizing the metal nanoparticles.

In [32] the representatives of non-traditional class of liquid crystals the ionic metal mesogens were investigated, which are the salts of mesogens, the salts of higher alkanoic acids forming thermotropic and lyotropic bilayer smectic meso-phase. The ion proper conductivity, high solvating power with respect to substances of different chemical nature, and a pronounced tendency to vitrification of the mesophases in the alkanoates of a number of metals makes them promising for the creation of new liquid crystalline materials for the optical electronics and laser technology. A rule of the ionic mesogeneity was formulated whereby the mesogenic properties can be displayed only by the metal alkanoates in which the metal is mono-, bi-, or tri-valent. On basis of the study of the phase equilibria in binary systems of metal alkanoates with a common anion or cation (more than 100 systems) the regularities of the formation of liquid crystalline solutions (continuous, boundary, and intermediate), and the optically anisotropic (mesomorphic) and isotropic glasses were revealed. 18 Major topological types of phase diagrams of binary systems of mesomorphic metal alkanoates were identified. It was found that mesomorphic glass of rare-earth metal alkanoates may be of non-porous structure and they may be a directionally-organized environment for the stabilization and orientation of nanoparticles of different chemical nature (fullerenes, nanotubes, organic dyes, metals, metal oxides, and chalcogenides). It was shown that the smectic structure of the alkanoate mesomorphic glasses provided a possibility to carry out high-rate holographic recording stipulating actuality of developing ionic liquid crystal materials for ultrafast optical switches in the telecom-munication optical-wave systems.

In [33–35] the surface-active properties of a series of salts with the 1-alkyl-3-methylimidazolium (mim) cation (alkyl is C_4, C_8 or C_{12}) and anion PF_6^-, BF_4^-, Cl^-, and Br^- were investigated. The dependence of surface activity from the temperature was studied using a ring tensiometer. Also, experiments were performed for revealing the structure and orientation of the ionic liquids surface. As established, the surface tension comprises an unusually wide range in the compounds of similar structure, namely, from 45 mJ m^{-2} for [bnim][PF_6] to 24 mJ m^{-2} for [C_{12}-mim][PF_6] at 336 K (bmim is 1-butyl-3-methylimidazolium). All of these ionic liquid salts exhibit a linear variation of surface tension with temperature, which allows the division of the surface indicators according to the excess entropy and energy. The surface tension (σ) of the studied ionic liquids, as revealed, is well described by a function decreasing linearly with the temperature:

$$\sigma(T) = a - bT$$

where a and b are the constants depending on the nature of the salt.

The values of excess parameters on the surface depend on the length of the alkyl chain. Both surface entropy (S_s) and energy (E_s) decrease with elongation of the alkyl chain of R^1 (position 1) in the cation when the anion is constant. For the same cation, the reduction in the size of the anion leads to lowering the surface entropy excess. In the same way the excess of the surface energy changes with decreasing anion size in the case of the same salts with shorter alkyl chains. Wide range of surface properties of these compounds probably reflects changes in the surface orientation of the cation.

The comparison of data on E_s and S_s for different substances shows that the measured values for the above ionic liquid salts are comparable with the corresponding values for some of neutral organic liquids, *n*-alkanes and heterocycles [36, 37]. The ionic liquid [bmim][PF_6] is comparable with the imidazole, and its surface energy is similar to that of such heterocycles as pyrrole and quinoline, but like the case of imidazole, its free surface entropy is much less. The surface entropy of the fluorine-containing ionic liquids salts except for [bmim][PF_6], is lower, and decreases with the lengthening of the alkyl chain. This decrease in surface entropy with increasing chain length is also observed in *n*-alkanes and is usually taken as an indicator of the increased degree of orientation at the surface [36].

The studied fluorinated ionic liquids salts exhibit surface energies close to those of the *n*-alkanes that are in the bottom of the range for organic liquids. These ionic liquids consist of large ions, which are sufficiently distant from each other. Consequently, we can expect that the Coulomb forces between them are relatively weak. When comparing ionic liquids salts with similar length of alkyl chain, it was found that surface energy was lower when the anions were smaller (BF_4^- compared with PF_6^- or Cl^- compared with Br^-).

The difference in surface energy decreases with increasing alkyl chain length and practically disappears at reaching the $C_{12}H_{25}$ chain. This suggests that with increasing size of the alkyl chain the effect of anion on the surface energy is quickly suppressed. Thus, in the case of ionic liquid salt with the cation [C_{12}-mim]$^+$ the surface energy is determined mainly by the cation, probably due to the increased van der Waals forces between the alkyl chains.

In [38] electroconductometric measurements of surface-active ionic liquid salts like [bmim][BTFMSI], [bmim][triflate] and [omim]·[triflate] {[bmim] = 1-butyl-3-methylimidazolium, [BTFMSI] = bis(trifluoromethylsulfonyl)imide, [omim] = 1-octyl-3-methylimidazolium} were carried out. The measurements were performed in the temperature range from 20 to 150°C. The specific conductivity of the last salt compared with the other two is found to be much lower, due to the large size of octyl chain in comparison with the butyl group. The calculated activation energy of specific conductivity increases when going from the first salt to the second and third. Raising the temperature within the above limits leads to a decrease in the activation energy of specific conductivity, which is associated with a decrease in viscosity of ionic liquids at heating. The calculations show that the difference between the activation energies of specific electrical conductivity of the first and second salts is 2.5–3.0 kJ mol^{-1}. The difference between the values for the third and second salts is much larger (5.0–7.0 kJ mol^{-1}).

The influence of the alkyl chain length in the cation and anion of 1-alkyl-3-methylimidazole (mim) alkylsulfonate salts of ionic liquids type with the formula $[C_nH_{2n+1}\text{-mim}][C_mH_{2m+1}SO_3]$ (in the first bracket 1-alkyl-3-methylimidazolium), where $n = 8$, 10, or 12, $m = 1$ and $n = 4$ or 8, $m = 4$ or 8, on the self-aggregation either in pure form or separately, in aqueous solution was studied [39]. Some of these ionic liquids represent a new family of ionic liquid surfactants with double chain. In the case of pure compounds, their strong tendency to self-aggregation led to the discovery of a liquid-crystalline phase in one of the representatives. Molecular modeling complements the study of the pure components and points to their self-separation at the nanoscale into clear-cut non-polar and polar domains in the liquid non-crystalline phase. In aqueous solutions of such ionic liquid surfactants the salts that contain an intermediate that includes long alkyl chains both in the cation and anion form pure cationic surfactants and behave like their real and effective representatives. Such surfactants are rare and differ from both the mixed cation-anion surfactant (formed by mixing of the two salts), and from the surfactant of the *gemini* type, in which there is an entropy limitation due to the chains attached to the same polar head group. Fluorescence spectroscopy and interfacial tension measurements allowed to determine the critical micelle-formation concentration, the surface activity, and to assess the effect of alkyl substitution in cations and anions on the surface properties of these salts. In the case of relatively small methylsulfonate anions ($n = 8$, 10 and 12, $m = 1$) the salts behave like normal cationic surfactant with one chain. At the same time a decrease in the critical micelle-formation concentration is observed with increasing alkyl chain length in the cation, that is, with increasing n. When the length of alkyl chains is the same in the cation and anion ($n = 4$, $m = 4$ and $n = 8$, $m = 8$), new cationic surfactants are formed with lower critical micelle-formation concentration values than for the corresponding cationic analogs, and whose surface tension is extremely lowered. Investigations of the thermotropic phase behavior of ionic liquids with the formula $[C_8H_{17}\text{-mim–H}]$ $[C_8H_{17}SO_3]$ ($n = m = 8$) using the methods of X-ray scattering at variable temperatures, polarizing optical microscopy, and differential scanning calorimetry showed the formation of a smectic liquid crystalline phase in a wide range of the temperature.

In [40] the dynamic surface tension of octadecyldimethylammonium chloride was measured, and it was shown that with increasing concentrations of ionic liquid surfactants the adsorption barrier increases. Similar results were described in [41]. These experimental facts can be explained as follows. At sufficiently low surfactant concentration its molecules can easily take up the space on the interface and the adsorption is instantaneous, that is, the limiting stage is diffusion. With increasing concentration, the number of the surfactant molecules adsorbed on the surface gradually increases and the surface pressure increases, which leads to appearance of the energy barrier [42, 43]. At this stage, mixed mechanism of diffusion-controlled adsorption dominates. Consequently, at high concentrations of surfactants, initially the adsorption is controlled by diffusion, and later this mechanism transforms to a mixed diffusion-adsorption [40–42].

In [44, 45] three surfactants of the ionic liquids nature namely, 1-dodecyl-3-methyl-imidazolium hexafluorophosphate ($[C_{12}\text{-mim}][PF_6]$), 1-tetradecyl-3-methylimidazolium-hexafluorophosphate ($[C_{14}\text{-mim}]$ $[PF_6]$), and 1-hexadecyl-3-methylimidazolium hexafluorophosphate ($[C_{16}\text{-mim}][PF_6]$) were used to form inclusion complexes with β-cyclodextrin. Measurements of surface tension showed that there are two types of inclusion complexes, with the components ratios β-cyclodextrin:ionic liquids 1:1 and 1:2 for β-cyclodextrin–$[C_{12}\text{-mim}][PF_6]$ and β-cyclodextrin–

[C_{14}-mim][PF_6], respectively, and only one type (1:1) for the complex β-cyclodextrin–[C_{16}-mim][PF_6]. These compounds were characterized by X-ray diffraction, ^{13}C and ^1H nuclear Overhauser effect, NMR spectroscopy, and TGA. The results obtained showed that these complexes are fine-crystalline powders. A channel-type structure was detected. It is suggested that the hydrophobicity is crucial for the formation of these inclusion complexes. The temperature of decomposition of the complexes is lower than that of the original components. The ability of the ionic liquids to form inclusion structures can be very useful for extraction of ionic liquids at the preparation.

The distribution–separation chromatographic columns coated with two alkylimidazolium ionic liquid salts with long alkyl chains ([C_{12}-mim]Br and [C_{14}-mim]Br) were used to perform separation of conventional inorganic anions [46]. These two salts are new cationic surfactants for ion chromatography. With the use of phthalate buffer solution as a mobile phase and detection without suppressing the conductivity a high efficiency and excellent selectivity of columns were achieved for the separation of inorganic anions. Calculated chromatographic parameters and the results show that the columns with such coatings have great potential for the analysis of anions like CH_3COO^-, IO_3^-, Cl^-, BrO_3^-, NO_2^-, NO_3^-, SO_4^{2-}, I^-, BF_4^- and SCN^-. On a column coated with [C_{12}-mim]Br the influence of the pH of the eluent on the separation of anions was studied. Also the stability of columns with such coating was studied.

Borisova et al. [47] investigated the surface-active ionic liquids salts of alkylimidazolium type, which contain alkyl groups of the linear structure C_{12} and C_{14}. Their aggregation in water and in aqueous phosphate buffer was studied spectrophotometrically. The values of the critical micelle-formation concentration for these salts were determined and compared with those of the cationic surface-active salts commonly used in capillary electrophoresis, like tetradecyl- and dodecyltrimethylammonium chlorides. The proposed salts are practically useful as a pseudo-stationary phase at the chromatographic separation of isomers of methylresorcynol and some benzene derivatives. One of the authors of that paper also has studied [48] the physicochemical properties of some ionic liquid salts containing the dialkylimidazolium cation.

The compound [C_{16}-mim]Br, which is also an ionic liquid, was used as a new cationic surfactant for the separation of phenolic compounds like hydroquinone, phloroglucinol, resorcinol, phenol, *p*-cresol, and *m*-nitrophenol by micellar electrokinetic capillary chromatography [49]. The effect of the buffer concentration and pH, the [C_{16}-mim]Br concentration, and the applied potential on the effectiveness of such separation was studied. Application of optimal buffer (NaH_2PO_4, 25 mM), at the concentration of [C_{16}-mim]Br 10 mM and the potential 15 kV allowed the optimum separation in terms of resolution and migration time. Phenolic compounds are detected at 214 nm. At their separation by this method the micelles of the used surface-active ionic liquids salt with a hexadecyl substituent act as a pseudo-stationary phase.

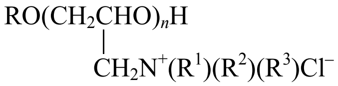
In [50] microemulsions were described with the ionic liquids serving as a surfactants, and the room-temperature ionic liquids (RTIL), as polar pseudophase. The microemulsions obtained contained the ionic liquids with a long alkyl chain, in particular [C_{16}-mim]Cl, as a surfactant, decanol, as a co-surfactant, dodecane, as a continuous phase, and RTIL, as a polar microsphere. As RTIL, ethylammonium nitrate and [bmim][BF_4] were taken separately. The phase diagrams of both systems were built at constant molar ratio of surfactant/co-surfactant. The method of electrocondutometry allowed to confirm the presence of the ethylammonium nitrate microareas in the oil. Zech et al. point to the possibility of application of the dynamic percolation model in the presence of ethylammonium nitrate. Measurements of dynamic light scattering evidence the swelling of the formed nanostructures with the increase in the ethylammonium nitrate content. A linear dependence was found of the hydrodynamic radius of these structures from the mass fraction of ethylammonium nitrate was found. Both systems exhibit a broad peak in the spectrum of small-angle X-ray scattering. The characteristic dependence of the scattering intensity (J) from the wavelength ($J \sim \lambda^{-4}$) for large λ values is observed. The Teubner–Stray model was used to determine the amphiphilic factor f_a and two characteristic values for the microemulsions, namely, the frequency d and the correlation length Σ. In addition, it was possible to determine the interface specific area. The amphiphilic factor clearly demonstrated the structural differences between the two systems, suggesting that the nature of the polar ionic liquids played an important role in the rigidity of the interfacial film. The applicability of three different models was verified, namely, the model of a spherical ionic liquids in oil, the model of repulsive spheres, and the model of double continuous structures.

The use of micelles based on the surface-active ionic liquids in the stationary phases for gas chromatography was estimated using equations derived for the "three-phase model" [51]. This model allows the determination of all three distribution coefficients in this system and revealing the micellar contribution to the retention and selectivity. In the study examined examined four types of micellar-ionic liquids columns are examined: [bmim]Cl with sodium dodecyl sulfate or dioctyl sulfosuccinate and [bmim][PF_6] with stearyl ether PEG-100 (that is, 100 units of ethylene oxide) or lauryl ether PEG-23 (that is, 23 ethylene oxide units). The distribution coefficients were measured for a wide range of the molecules that are prone to various types of interactions in different degrees. In general, most of the examined molecules are distributed mainly in the micellar pseudophase located above the main part of the ionic liquid component of the stationary phase. Hence, the addition of the surfactant in the stationary phase usually leads to a greater retention of solute. Also it was shown that the selectivity of the stationary phase varies considerably in the presence of micelles due to either intensifying or slowing of the separation. The surfactant action on the interaction parameters in the stationary phase was determined using the Abraham's model which takes into account the solvation parameter. Adding sodium dodecyl sulfate or dioctyl sulfosuccinate to the stationary phase with [bmim]Cl in general increases the basicity of the hydrogen bond of the phase and increases the level of dispersion interaction. However, PEG-100 stearyl ether and PEG-23 lauryl ether being surfactants increase π–π and n–π interaction, polarizability, and polarity of the dipole and the interactions of [bmim][PF_6] as a result of the basicity of the hydrogen bond to a greater extent than ionic surfactants on the basis of [bmim]Cl. These nonionic surfactants reduce the ability of the stationary phase to interact with solutes through dispersion forces. Consequently, it is possible to predict reliably which of the analyzed substances will be retained particularly strongly by these micellar ionic liquid stationary phases.

Baghdadi et al. [52] have developed a new technique for microextraction with surface-active ionic liquids named a microextraction with the solvent formed *in situ*. A small amount of sodium hexafluorophosphate ($NaPF_6$) used as an agent for the ion pairing is added to the sample solution containing a very small amount of 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim][BF_4]) as a hydrophilic surface-active ionic liquid. A turbid solution is formed due to the formation of small droplets of [hmim][BF_4]. After centrifugation, the fine droplets of extractant phase fall to the bottom.

This is a simple and fast extraction method for the pre-concentration of metal ions from aqueous samples. It can also be applied to a solution containing a salt in a very high concentration. In addition, the method is much safer compared to the extraction with an organic solvent. The reliability of the developed method was estimated by analyzing a standard aqueous solution. The method was successfully used for the determination of Hg(II) in several water samples. The type and amount of surface active ionic liquids, temperature and other parameters were optimized. Under optimal conditions, the limit of detection was found to be 0.7 ng ml^{-1} and relative standard deviation 1.94% at a concentration of Hg 40 ng ml^{-1}.

In the Institute of Petrochemical Processes of National Academy of Sciences of Azerbaijan a series of new ionic liquids surfactants was synthesized. The quaternary salts were prepared from the higher aliphatic alcohols (C_9–C_{14}), epichlorohydrin, and (alkanol)amines. In the first stage of the catalytic condensation of alcohol and epichlorohydrin the respective oligomeric chloromethyl-substituted polyether is formed which gives a quaternary salt in the quaternization reaction with a compound containing an amino group [53–59]:



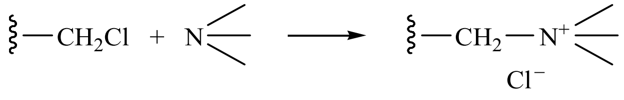
$$\mathrm{RO(CH_2\underset{\displaystyle |\atop \displaystyle CH_2N^+(R^1)(R^2)(R^3)Cl^-}{CH}O)}_n\mathrm{H}$$

where R = C_9–C_{14}, n is the degree of oligomerization, R_1, R_2 and R_3 = H, CH_3, C_2H_5, C_2H_4OH, C_3H_6OH (depending on the used alkanolamine and amine): R_1–R_3 may together form a cyclic system (as in the case of pyridine and piperidine).

Among the alkanolamines mono-, di-, and triethanolamine, methylaminoetanol and propanolamine, as amines diethylamine, pyridine, and piperidine were used. The quaternary salts were characterized by physicochemical parameters like density, refractive index, and extinction coefficient (ε), hydrophilic-lipophilic balance calculated by the system of Davies, the specific conductivity (χ), hydroxyl number, the surface tension (σ) for the water–air and the water–kerosene boundaries.

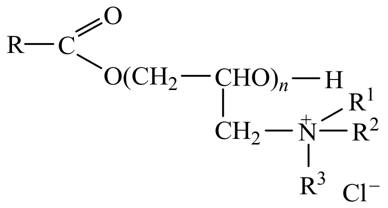
The most surface-active on the kerosene–water boundary (without a surfactant $\sigma = 46.0–46.5$ mN m^{-1}) is the oligoether ($n = 2.5$) from epichlorohydrin and decanol quaternized with triethylamine ($\sigma_{0.5–1.0\%} = 5.5$ mN m^{-1}) as well as methylaminoethanol salt of the oligoether ($n = 7.1$) from epichlorohydrin and nonanol ($\sigma_{0.5–1.0\%} = 5.5$ mN m^{-1}) and oligoether ($n = 4.6$) from epichlorohydrin and dodecanol quaternized with diethanolamine ($\sigma_{1.0\%} = 5.5$ mN m^{-1}). The ε parameter of the quaternary salts is 1.3–1.9 times higher than that of the initial chloromethyl derivative. The χ parameter of the 0.5 wt % aqueous solutions of the salts is in the range from 0.0100 to 1.9100 Ω^{-1} m^{-1} that is much higher than for distilled water itself (0.001–0.0001 Ω^{-1} m^{-1}). Identification of the composition and structure of the obtained compounds was carried out by ^{1}H NMR, IR, and UV spectroscopy. Most of the quaternary salts and their 5 wt % aqueous solutions (dispersions) show the oil-collecting or dispersing properties on the water surface [60, 61].

The ionic liquid salts were obtained [56, 62–64] also on the basis of aliphatic polyols, epichlorohydrin, and (ethanol)amines. As the polyols ethylene glycol, 1,2-propylene glycol, 1,3-butylene glycol, and glycerol were used, amines were diethanolamine, pyridine and piperidine, ethanolamines comprise mono-, di-, and triethanolamine. In the first stage by the catalytic reaction of alcohol with epichlorohydrin oligomeric ethers were synthesized. In the second stage the chloromethyl-polyether reacted with the nitrogen base according to the quaternization reaction. As a result the ammonium salts of the ionic liquids type were synthesized.



Study of physicochemical parameters of the synthesized ammonium salts showed that their χ parameters (from 0.0023 to 0.1830 Ω^{-1} m^{-1}) are much larger than χ of distilled water. The composition and structure of synthesized ionic liquids salts were investigated by various spectroscopic methods. Stalagmometric investigations of the water–kerosene interface with the synthesized ionic liquids salts have revealed high surface activity of the latters. At the 5% concentration of triethylammonium salt of the chloromethylate polyester with glycerol ($n = 26.2$) it is found that $\sigma = 2.0$ mN m^{-1}. Laboratory tests [60, 61] revealed the ability of ionic liquid ammonium salts synthesized from C_2–C_4 polyols, epichlorohydrin and ethanolamines to slow down evaporation of gasoline at storage.

On the basis of individual saturated monocarboxylic acids, epichlorohydrin, amines, and alkanolamines (including mono-, di-, and triethanolamine, methylaminoethanol, propanolamine, diethylamine, pyridine, and piperidine) the respective quaternary salts were produced [53, 55–57, 65–70].



Here R = C_6–C_{10}, C_{15}, C_{17}; n is the degree of chloroxypropylation, R_1, R_2 and R_3 are H, CH_3, C_2H_5, C_2H_4OH and C_3H_6OH; R_1–R_3 together may form a cyclic system.

As the saturated monocarboxylic acids, the linear monocarboxylic acids C_7–C_{11}, C_{16} and C_{18} were used. The χ parameters of aqueous solutions of most of these salts are much higher than this quantity for water, indicating their ionic liquid structure. Composition and structure of these salts were studied with the above-mentioned spectral methods. The values of σ of 0.5 wt % aqueous solutions are illustrative of their large surface activity on the kerosene–water border (σ is equal to 0.8–15.1 mN m^{-1}). The resulting quaternary salts have the properties of oil collection and dispersing ability.

Cationic surfactants were obtained [65, 69, 71, 72] also on the basis of ethanolamine and chloromethyl derivatives of esters of the acid fractions isolated from a number of vegetable oils by alkaline hydrolysis described in detail in [73–75]. As the oils castor, olive, linseed, cottonseed, and soybean oils were used, and ethanolamines were mono-, di-, and triethanolamine. High values of χ of the 0.5% water solutions as compared with water indicate the ionic structure of the resulting products. The highest surface activity on the kerosene–water border was shown by diethanolamine salt of the acid fraction of castor oil and triethanolamine salt of the acid fraction of olive oil ($\sigma = 3.6$ mN m^{-1} at a concentration of 0.5 wt %). The identification of the composition and structure of the resulting products was carried out by the above-considered spectroscopic methods. The resulting salts exhibit the oil-collecting and dispersing properties.

The complexes of natural fractions of the carboxylic acids extracted from natural natural lipids with mono-, di-, and triethanolamine as well as quaternary salts obtained from these fractions, epichlorohydrin and the ethanolamines, which are the substances of ionic liquid nature, show strong inhibitory properties with respect to the steel corrosion in acidic medium [71].

In the reaction of capric and tridecanoic acids as well as the acidic fractions of castor, cotton, corn, linseed, and sunflower oils with the above ethanolamines the ethanolaminocarboxylate complexes of ionic liquid type were synthesized [72]. They were identified by the methods of ^{1}H NMR, IR, and UV spectroscopy and characterized by various physicochemical parameters. Complexes of individual monocarboxylic acids with ethanolamines reduce the σ parameter on the kerosene–water boundary from 46.0–46.5 to 1.8–2.7 mN m^{-1}, and the complexes of acidic fractions with ethanolamines up to 1.5–2.7 mN m^{-1}. These complexes exhibit fairly high oil-collecting and dispersing abilities. The complexes of ethanolamines with acid fractions of castor, sunflower, and soybean oils were found to have the property to slow down the steel corrosion in acid medium considerably. In addition, these complexes of the acidic fractions and the quaternary salts obtained by the modification of the chloromethyl derivatives of polyesters obtained from these fractions through quarternization reaction of chloromethyl groups in the oligomeric matrix with ethanolamines enable to collect or disperse the oil film on the water surface [53, 71, 72]. The ability of the ionic liquids derived from ethanolamine and acid fractions of castor and sunflower oils to the extraction of aromatic compounds [72] was also revealed.

The quaternary salts of the type of cationic surfactants were synthesized on the basis of ethanolamines and alkyl halides [55, 56, 65,76–80]. The ethanolamines used were mono-, di- and triethanolamines and dimethylaminoethanol. The alkyl halides were *n*-decyl bromide, *n*-heptyl iodide, and *n*-pentyl bromide. Quaternization reactions resulted in the compounds of general formula $(R^1)(R^2)(R^3)(R)N^+ X^-$, where R is alkyl group (C_5, C_7 and C_{10}); R^1, R^2, and R^3 are H, CH_3, and C_2H_4OH groups, and X^- is Br^- and I^- anions. The values of χ ($\chi_{0.5\%} = 0.0075–0.092\ \Omega^{-1}\ m^{-1}$) for the synthesized salts in combination with the measured freezing points are a tangible proof of their ionic liquid structure. These compounds have good surface activity at the water–kerosene boundary, but the salts based on the decyl bromide and heptyl iodide are especially active: they reduce the interfacial tension to 1–2 mN m^{-1}, and even at very low concentrations (0.05 wt %) to ultra-low values (practically to zero). Noteworthy is the fact of very good solubility in water of the decyl bromide salts with mono-, di-, and trietanolamines (even 50% aqueous solution can be obtained). The composition and structure of the quaternary salts obtained were confirmed by the ^{1}H NMR, IR, and UV spectroscopy.

Studies of the oil-collecting and dispersing ability of these salts showed that the salts with decyl bromide and in part with heptyl iodide are mostly active. Comparison of the data obtained indicates the importance of the length of the alkyl radical. However, this condition is not sufficient. Experiments with a specially synthesized salt of diethylamine with decyl bromide $HN^+(C_2H_5)_2C_{10}H_{21}\,Br^-$ showed lack of the oil-collecting and dispersing properties. This is explained by the absence of a hydroxy group in the salt, which apparently plays an important role in the collecting or dispersing action. Such action is inextricably associated with the ability of surfactants to the micelle formation in particular conditions of its application with accounting for its working concentration.

Some cationic surfactants were synthesized by the quaternization reaction from octadecylamine and alkyl halides, with the formula $C_{18}H_{37}NH_2(R)X$, where R is alkyl, X^- is halide (iodide or bromide) anion [55, 56, 81]. As the alkyl halide methyl iodide, propyl iodide, butyl iodide, pentyl bromide, and heptyl iodide were used. The composition and structure of the quaternary salts obtained were confirmed by IR and UV spectroscopy. The methyl-, propyl-, butyl-, and heptyloctadecyl-ammonium iodides at ambient conditions are pale-yellow solid substances that can be easily pulverized to form powder. The pentyloctadecylammonium bromide is a milky-white solid (at ambient conditions), also capable to be pulverized. The methyl derivative is dispersed in water and dissolved under heating. Propyl, butyl, heptyl, and pentyl derivatives are insoluble in water but soluble in ethanol. The pentyloctadecyl-ammonium bromide melts at 55.5°C, the heptyl derivative, at 65°C. Due to the presence of a very long alkyl radical (C_{18}) and a polar NH_2 fragment (the analog of OH groups in the salts of the fourth group), these products exhibit fairly high efficiency in collecting and dispersing the oil films.

From the foregoing it is clear that the interest in the ionic liquids with a surface-active properties both from scientific and practical viewpoints was growing in recent years. This is due to a large variety of their composition (anionic, cationic, and catanionic ionic liquids) and a wide range of their practical properties.

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