Regular Article

PHYSICAL
CHEMISTRY
RESEARCH

Published by the
Iranian Chemical Society
www.physchemres.org
info@physchemres.org

Phys. Chem. Res., *Vol. 2, No. 2, 159-170 , December 2014.*
DOI: 10.22036/pcr.2014.5483

Vapor-Pressure Osmometry and Conductivity Determination of Salting-Out Effects in Aqueous Surface-Active Ionic Liquid 1-Dodecyl-3-methylimidazolium Bromide Solutions

R. Golabiazar and R. Sadeghi*

Department of Chemistry, University of Kurdistan, Sanandaj, Iran

(Received 6 February 2014, Accepted 4 May 2014)

Systematic studies on the vapor-liquid equilibria (VLE) and conductometric properties of aqueous solutions of model surface-active ionic liquid 1-dodecyl-3-methylimidazolium bromide ([C_{12}mim]Br) are performed in the absence and presence of a large series of electrolytes in order to achieve a deeper understanding about the molecular mechanism behind the specific salt effect on the aggregation behavior of [C_{12}mim]Br in aqueous solutions. For this purpose, six chloride electrolytes (NaCl, KCl, NH_4Cl, $(CH_3)_4NCl$, $MgCl_2$ and $FeCl_3$) and five sodium electrolytes (NaCl, $NaNO_3$, Na_2CO_3, Na_2SO_4 and Na_3Cit.) were used to individualize the effects of the anion and cation. The values of the critical aggregation concentration (CAC) were obtained and it was found that all the investigated electrolytes have salting-out effect on the aggregation of [C_{12}mim]Br in aqueous solutions, leading to significant downward shifts of the CAC. The magnitude of the shifts depends on the water-structuring nature of the electrolyte and follows the Hofmeister series. Furthermore the effect of electrolyte on the degree of anionic binding and thermodynamic parameters of aggregation for [C_{12}mim]Br in aqueous solutions were determined.

Keywords: Ionic liquid, Aggregation, Vapor-pressure osmometery, Conductivity, Salt effect

INTRODUCTION

Ionic liquids (ILs), organic salts with melting temperature below 373.15 K, are perspective for applications in various fields of chemistry and technology. They determine their importance for green chemistry because of their unique properties such as wide liquid state range, low volatility, non-flammability, high thermal stability, low toxicity, high ionic conductivity, wide electrochemical window, enhanced reaction rates obtained in ILs, high ability to dissolve an enormous number of materials, and *etc*. The salts composed of 1-alkyl-3-methylimidazolium cation $[C_n\text{mim}]^+$ are one of the most important classes of ILs which have received much attention and have been extensively studied [1]. An interesting aspect of such ILs is that similar to classical surfactants, they consist of a charged hydrophilic head group and a hydrophobic tail and therefore they could possess an inherent amphiphilic nature and form micelles in aqueous solution when their alkyl group is a longer hydrocarbon chain. Environmental pollution treatment, preparation of nanostructured materials, synthesis of reversible solvent-induced porous polymers, and applications from battery design to reaction controlled by surface active ionic liquids (SAILs) are closely dependent on such aggregation behavior [2]. Therefore, self-aggregation behavior of SAILs as a novel class of surfactants has aroused much interest for the understanding of how IL participates in practical applications as a component and in the past several years a number of researchers have investigated the self-aggregation behavior of SAILs in aqueous solutions [3-35]. The aggregation of ionic surfactants in aqueous solutions is influenced by the electrostatic interactions between the ionized head groups and their interactions with the surrounding counterions and water molecules. Salts normally reduce the electrostatic

---

*Corresponding authors. E-mail: rsadeghi@uok.ac.ir repulsion among the surfactant head groups and therefore decrease the critical aggregation concentration (CAC) of ionic surfactants (salting-out effect). Although the effects of salt on the aggregation behaviors of SAILs in aqueous solutions are vital to many applications for detergency and emulsification in industry, very limited information has been reported in the literature in this respect. Furthermore, although downward shifts of the CAC of ILs by adding salts are documented, there still exits considerable uncertainty to the details of the mechanism of these effects. In this context, Rebelo *et al.* [10] found that the salts NaCl, Na_2SO_4 and tetrabutylammonium bromide have salting-out effects on the CAC values of $[C_{10}mim]Cl$ and $[C_{12}mim]Cl$ in aqueous solutions and the CAC values are decreased with increasing ionic strength of the added salts. Dong *et al.* [11] also found that the CAC values of $[C_{10}mim]Br$, $[C_{12}mim]Br$ and $[C_{12}mim][BF_4]$ in aqueous solutions are decreased in the presence of the salts NaCl, NaBr and NaI and the effects of anions in the salting-out effect of the investigated ILs are decreased in the order $I^- > Br^- > Cl^-$. Recently, Wang *et al.* [36] investigated the influence of a series of 15 salts on the aggregation behavior of $[C_{10}mim]Br$ in aqueous solutions by conductivity, fluorescence, and dynamic light scattering at 298.15 K. They showed that two bromide salts, $FeBr_3$ and $AlBr_3$, have salting-in effect, whereas other investigated sodium salts have salting-out effect on the aggregation of $[C_{10}mim]Br$ in aqueous solutions, and the ability of the anions to promote aggregation of the IL was found to increase in the order: $SCN^- > I^- > C_6H_5COO^- > ClO_3^- > NO_3^- \approx C_4H_4O_6^{2-} > C_6H_5O_7^{3-} > Br^- > SO_4^{2-} > CO_3^{2-} > Cl^- > BrO_3^- > CH_3COO^-$. However, up to this date, there are no exhaustive studies that examine the influence of electrolytes on the vapor-liquid equilibria (VLE) behavior of SAIL-aggregates and considerable uncertainty remains about the details of the mechanism of salt effects on the aggregation behavior and thermodynamic properties of surfactant-like ILs in water. In fact, the activity of water is one of the most important thermodynamic properties for understanding of the interactions in aqueous solutions. In addition, the activity is closely related to the other thermodynamic properties, and also is an essential variable in thermodynamic modeling. The water activity in different aqueous solutions is strongly affected by the solute-water interactions. Thus, if the mechanism of the salting effects involves dehydration of the SAIL or association of ions with SAIL, the water activity is be expected to be strongly dependent on different ions. Furthermore, although the concentration dependence of the different properties exhibit a change in slope at the concentration in which micelles are formed, the concentration dependence of VLE properties exhibits a more distinct change. And yet, in spite of all these considerations, the VLE properties have not been used for the studying of the salt effect in aqueous SAIL solutions.

Therefore, in an attempt to obtain further evidence about the salting effect produced by the addition of different salts to aqueous solutions of SAILs and make a thorough analysis of the salting-out effects of different anions and cations on the aggregation behavior of a surfactant-like IL, $[C_{12}mim]Br$, in aqueous medium, this work is, mainly focused on (i) the study of the VLE properties of solutions of $[C_{12}mim]Br$ in water and in aqueous solutions of electrolytes KCl, NH_4Cl, $(CH_3)_4NCl$, $MgCl_2$, $FeCl_3$, NaCl, $NaNO_3$, Na_2CO_3, Na_2SO_4, and Na_3Cit. at 308.15 K, (ii) the study of effects of the mentioned salts as well as temperature on the conductivity properties of aqueous solutions of $[C_{12}mim]Br$.

EXPERIMENTAL

Materials

$[C_{12}mim]Br$ was purchased from Iolitec GmbH. KCl, NH_4Cl, $(CH_3)_4NCl$, $MgCl_2$, $FeCl_3$, NaCl, $NaNO_3$, Na_2CO_3, Na_2SO_4 and Na_3Cit were purchased from Merck. $[C_{12}mim][Br]$ was dried in high vacuum at 333.15 K using a rotary evaporator for at least 4 h in 0.7 kPa. The moisture of $[C_{12}mim]Br$ was controlled by Karl Fischer method during the experimental method. Double distilled and deionized water was used.

Experimental Procedures

All the solutions were prepared by mass on a Sartorius CP225D balance precisely within $\pm 1 \times 10^{-8}$ kg. Electrical conductivities were measured by a digital conductivity meter (Metrohm model 712) with a sensitivity of 0.1% and a dipping-type conductivity cell with platinized electrodes at a frequency of 1 MHz. A cell constant of 0.855 cm^{-1} was determined by the calibration of cell with 0.01 mol dm^{-3} aqueous KCl solutions. All measurements were performed in a double-walled glass container at a certain temperature maintained by a Julabo circulating thermostat with a precision of 0.02 K. The conductivities measurements of the investigated solutions were carried out by continuous addition of a concentrated [C_{12}mim]Br solution into a known quantity of solvent (salt aqueous solutions) taken in the container. The conductivity was recorded when its fluctuation was less than 1% within 2 min. The total uncertainty for this property is 0.1 S cm^2 mol^{-1}.

In this study, the vapor pressure osmometry (VPO) method was used to obtain the water activities of the investigated [C_{12}mim]Br solutions. The VPO was performed with the help of an Osmomat K-7000 (Knauer Inc.). The details of the VPO method are similar to the one used previously [37]. The measuring chamber of osmometer contains a reservoir of water, paper wicks to provide a saturated water atmosphere and two thermistors that are placed in an airtight cell which measure resistance changes caused by changes in temperature. Firstly, a droplet of pure water is attached to each thermistor with the help of a microsyringe, and after 5 min of equilibration, the reading is adjusted to zero. Then, the pure water on one thermistor is replaced by the [C_{12}mim]Br + salt aqueous solution and condensation of water from the vapor phase into the [C_{12}mim]Br + salt solution at the thermistor takes place. Due to the heat of condensation, the thermistor containing [C_{12}mim]Br + salt solution will be warmed and vapor pressure rises. These processes continue until the vapor pressure of the [C_{12}mim]Br + salt solution equals the vapor pressure of the pure water. The change in temperature changes the resistance of the thermistors. A bridge circuit measures the resistance difference of both thermistors. As long as changes in temperature are small, the resistance is proportional to ΔT. Generally, a time of 4-8 min suffices to reach this steady state. First, the instrument was calibrated using aqueous NaCl solutions as reference with known osmotic coefficients in the proper concentration range, yielding a function that correlates the panel readings to the corresponding concentrations of the reference solutions and therefore their osmotic coefficients. Then, in the same conditions, the panel readings were measured for the studied [C_{12}mim]Br + salt solutions. For each solution, at least five determinations (zero point adjustment and new solution) were performed and the mean value is reported. Generally, the deviations from the mean value were less than 1%. The cell temperature, which is electronically controlled, has a standard uncertainty of $\pm 1.10^{-3}$ K. For a certain [C_{12}mim]Br/salt solution which has a same instrument reading as a sodium chloride solution with molality m_{NaCl} and osmotic coefficient Φ_{NaCl}, the osmotic coefficient Φ was obtained according to:

$$\Phi = \left(\nu_{NaCl} m_{NaCl} \Phi_{NaCl}\right) / \left(\nu_{IL} m_{IL} + \nu_{salt} m_{salt}\right) \tag{1}$$

where, m_{IL} is molality of the ionic liquid, ν is the stoichiometric number and subscripts IL and salt stand for [C_{12}mim]Br and salt, respectively. Φ_{NaCl} is the osmotic coefficient for aqueous solutions of NaCl with molality m_{NaCl} calculated from the correlation given in the literature [38]. From the experimental osmotic coefficients, it is possible to calculate the water activities of the investigated solutions using the following relation:

$$a_w = \exp\left[-M_w\left(\nu_{IL} m_{IL} + \nu_{salt} m_{salt}\right)\Phi\right] \tag{2}$$

where M_{w} is the molar mass of water. The uncertainty in the measurement of water activity was found to be better than ± 2 × 10^{-4}.

RESULTS AND DISCUSSION

In this work, two sets of experiments with more than 1400 different measured data were carried out in order to achieve further understanding about the salting effect produced by the addition of different salts to aqueous solutions of [C_{12}mim]Br. Toward this end, 6 chloride salts (NaCl, KCl, NH_4Cl, $(CH_3)_4NCl$, $MgCl_2$ and $FeCl_3$) and 5 sodium salts (NaCl, $NaNO_3$, Na_2CO_3, Na_2SO_4, and Na_3Cit.) were used in order to individualize the effect of the anion and cation and the VPO measurements at 308.15 K and electrical conductivity measurements at 298.15, 303.15, 308.15 and 313.15 K were carried out for the aqueous solutions of [C_{12}mim]Br in the absence and presence of 0.035 mol kg^{-1} investigated salts. In order to obtain further information about the salting-out of SAIL [C_{12}mim]Br by electrolytes, and to obtain a relation between the VLE behavior and salting-out effects in aqueous [C_{12}mim]Br solutions, the vapor-pressure osmometry measurements of water activity were carried out for solutions of [C_{12}mim]Br in water and in aqueous solutions of 0.035 mol·kg^{-1} electrolytes KCl, NH_4Cl, $(CH_3)_4NCl$, $MgCl_2$, $FeCl_3$, NaCl, $NaNO_3$, Na_2CO_3, Na_2SO_4 and Na_3Cit at 308.15 K. The water activity in different aqueous solutions is strongly affected by the solute-water interactions. Thus, if the mechanism of the salting effects involves dehydration of the [C_{12}mim]Br or association of ions with SAIL, the water activity is be expected to be strongly dependent on different ions.

Vapor-Liquid Equilibria Properties

As seen in Fig. 1, the plots of water activity against molality of [C_{12}mim]Br exhibit a change in slope at the concentration in which micelles are formed. For m_{IL} > CAC, water activity is larger than those we expect in the case of supposed monomer solutions (hypothetical monomeric solutions with m_{IL} > CAC which have been shown by dotted lines in Fig. 1a). The concentration dependence of water activity for solutions with m_{IL} < CAC is more negative than that with m_{IL} > CAC indicating that the water-monomer interaction must be of a more stable nature than water-micelle interaction. In fact, because of the binding of a fraction of the counter ions to the micellar surface, ionic charges as well as the hydration number reduce and therefore for a certain [C_{12}mim]Br concentration, both of water activity and vapor pressure depression of micellar solutions of [C_{12}mim]Br are larger than those we expect in the case of supposed monomer solutions. Figure 1 also shows that water activities for the investigated solutions follow the order: [C_{12}mim]Br in pure water > [C_{12}mim]Br in aqueous solutions of 1:1 electrolytes > [C_{12}mim]Br in aqueous solutions of 2:1 and 1:2 electrolytes > [C_{12}mim]Br in aqueous solutions of 1:3 electrolytes > [C_{12}mim]Br in aqueous solutions of 3:1 electrolytes and these differences increase by increasing SAIL concentration. The higher valence ions hydrate more water molecules than the lower valence ions and therefore we may expect that the solutions of [C_{12}mim]Br in aqueous solutions of 0.035 mol kg^{-1} electrolytes with higher valence ions, because of the stronger ion-water interactions, have smaller water activities than those of lower valence ions. The differences between water activities of the investigated solutions and those of their solvents (water and aqueous solutions of 0.035 mol kg^{-1} electrolytes) have been shown in Fig. 1b. As can bee seen, this figure has a same behavior with that of water activity (Fig. 1a). From the experimental water activity data, the values of vapor pressure data of different solutions were determined with the help the following relation:

$$\ln a_w = \ln\left(\frac{p}{p_w^\circ}\right) + \frac{\left(B_w^\circ - V_w^\circ\right)\left(p - p_w^\circ\right)}{RT} \qquad (3)$$

where B_w° is the second virial coefficient of water vapor, V_w° is the molar volume of liquid water, and p_w° is the vapor pressure of pure water. Figure 1c shows the differences between the vapor pressure depression (Δp) of the investigated solutions and those of their solvents (water and aqueous solutions of 0.035 mol kg^{-1} electrolytes). As can bee seen, this figure has a same behavior with that of water activity. Figure 1 shows that the vapor pressure depression for a ternary solution is larger than the sum of those for the corresponding binary solutions and in the micellar solutions this difference increases as charge on the ions of electrolyte increases.

By assuming the similar standard state for the micellar and supposed monomer solutions, the free Gibbs energy for transfer of x_w moles of water from the supposed monomer solutions to the real micellar solutions, ΔG_w^{mic}, can be obtained from the following equation:

$$\Delta G_w^{mic} = x_w(\mu_w^{mic} - \mu_w^{mon}) = x_w RT \ln \frac{a_w^{mic}(T,P,m)}{a_w^{mon}(T,P,m)} \qquad (4)$$

where μ_w is the chemical potential of water and superscripts *mic* and *mon* stand for the micellar and supposed monomer solutions, respectively. The calculated values of the free energy of micellization are shown in Fig. 2a. The small positive values of ΔG_w^{mic} indicate that the water molecules in the supposed monomer solutions are slightly more stable than those in the real micellar solutions. Since the micellization of [C_{12}mim]Br in water and in aqueous electrolyte solutions is a spontaneous process, therefore we expect the large negative values for ΔG_{IL}^{mic} which indicate that [C_{12}mim]Br ions in the micellar solutions are more stable than those in the supposed monomer solutions. The values of ΔG_{IL}^{mic} should be large

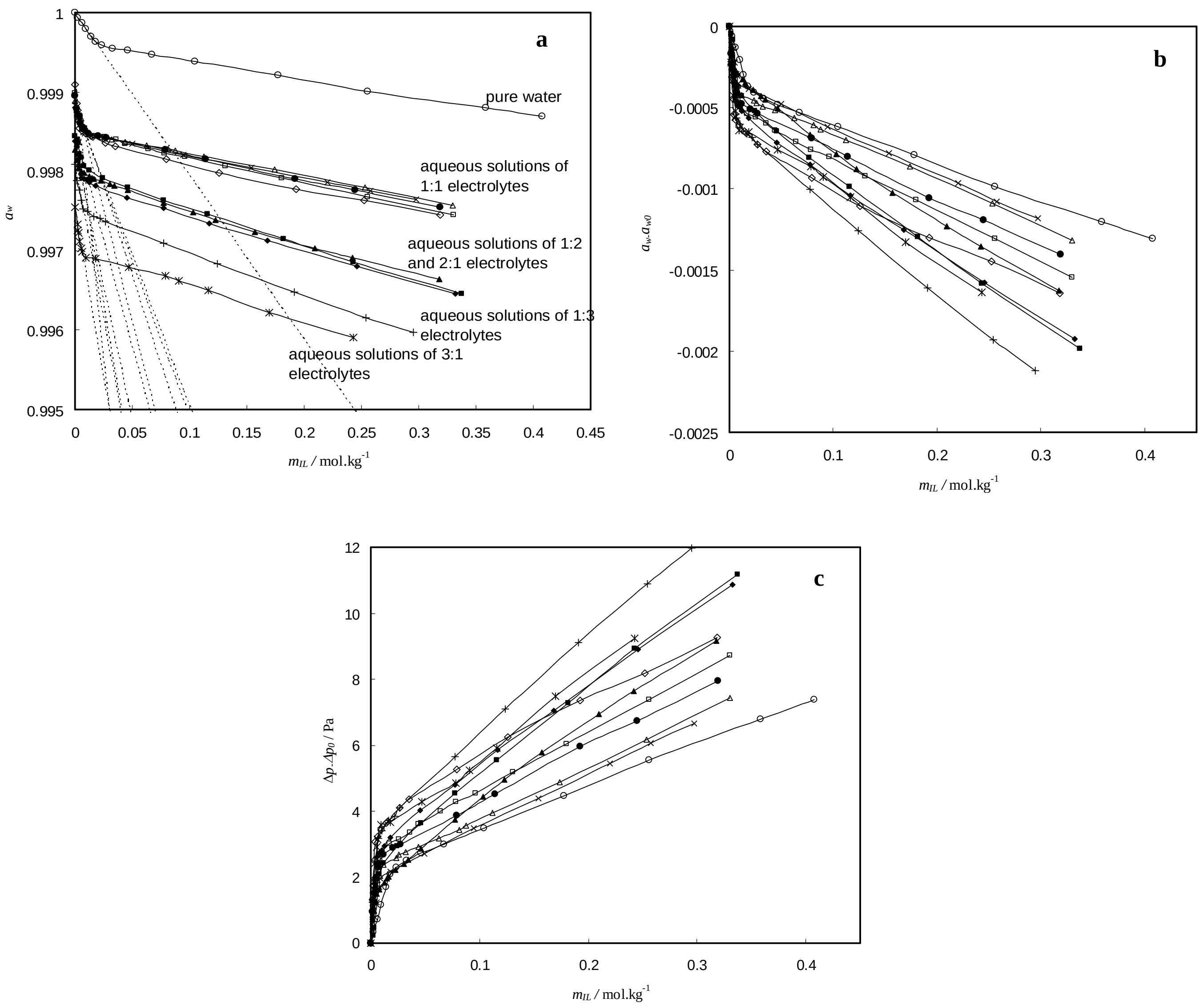

Fig. 1. Plot of a_w (a), $a_w - a_{w0}$ (b), and $\Delta p - \Delta p_0$ (c), against molality of [C$_{12}$mim]Br, m_{IL}, for [C$_{12}$mim]Br in water and in aqueous solutions of 0.035 mol kg^{-1} electrolytes: ○, pure water; △, NaCl; □, KCl; ◇, NH$_4$Cl; ×, (CH$_3$)$_4$NCl; ●, NaNO$_3$; ▲, MgCl$_2$; ■, Na$_2$CO$_3$; ◆, Na$_2$SO$_4$; +, Na$_3$Cit; *, FeCl$_3$; …, Supposed monomer solution.

and negative so that despite the positively calculated values for ΔG_w^{mic}, the calculated free energies of micellization (ΔG_{IL}^{mic} + ΔG_w^{mic}) have negative values. Increasing the chemical potential of water upon micellization indicates that the SAIL-water interactions in the supposed monomer solutions are stronger than those in the corresponding real micellar solutions. The values of ΔG_w^{mic} for the investigated solutions follow the order: pure water < NaCl < Na$_2$CO$_3$ < NaNO$_3$ < Na$_3$Cit < Na$_2$SO$_4$ for sodium electrolytes and pure water < (CH$_3$)$_4$NCl < NaCl < KCl < MgCl$_2$ < FeCl$_3$ < NH$_4$Cl for chloride electrolytes.

When a solution of 0.035 moles of electrolytes in 1 kg of water is isothermally mixed with a solution of m_{IL} moles of [C$_{12}$mim]Br in 1 kg of water, and then 1 kg of liquid

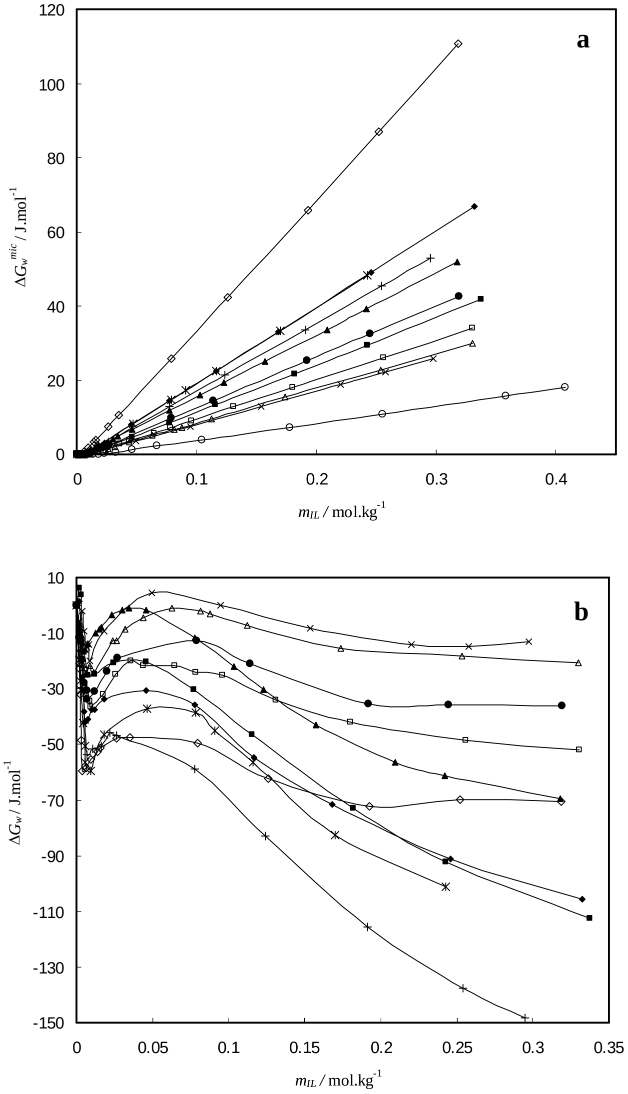

Fig. 2. Plot of ΔG_w^{mic} (a) and ΔG_w (b) against molality of $[C_{12}mim]Br$, m_{IL}, for $[C_{12}mim]Br$ in water and in aqueous solutions of 0.035 mol kg^{-1} electrolytes: ○, pure water; △, NaCl; □, KCl; ◇, NH_4Cl; ×, $(CH_3)_4NCl$; ●, $NaNO_3$; ▲, $MgCl_2$; ■, Na_2CO_3; ◆, Na_2SO_4; +, Na_3Cit; *, $FeCl_3$.

water is isothermally separated via an osmotic membrane, the free energy change of the water can be obtained from the following equation

$$\Delta G_w = 55.51RT\ln\left(\frac{a_w}{a_w^{\circ s}a_w^{\circ IL}}\right) \tag{5}$$

where $a_w^{\circ s}$ is the water activity in a binary electrolyte + water solution at molality 0.035; $a_w^{\circ IL}$ is that in a binary $[C_{12}mim]Br$ + water solution at molality m_{IL}; a_w is that in a ternary electrolyte + $[C_{12}mim]Br$ + water solution containing electrolyte at molality 0.035 and IL at molality m_{IL}. The calculated values of ΔG_w are shown in Fig. 2b. As can be seen, the values of ΔG_w for the investigated systems are negative and their magnitudes are increased by increasing charge on the anion and cation of electrolytes.

Conductometric Properties

Figure 3 illustrates the typical plots of specific and molar conductivity *vs.* molality for solutions of $[C_{12}mim]Br$ in water and in aqueous solutions of 0.035 mol kg^{-1} electrolytes at 298.15 K. The similar behavior was obtained for other temperatures.

As can be seen, the plots for the specific conductivity show linear behavior with two different positive slopes at the concentrations below and above the CAC at which a pseudophase transition takes place between monomers and micelles. Above the CAC, the augmentation of the specific conductivity has a smaller slope because of two reasons: (i) the confinement of a fraction of the counterions to the micellar surface results in an effective loss of ionic charges and (ii) the micelles can contribute to the charge transport to a lesser extent than the free ions owing to their lower mobility [39]. Close examination of the experimental specific conductivity data in the large $[C_{12}mim]Br$ concentration range shows that (as can be seen from Fig. 4), in the presence of electrolytes, the plots of specific conductivity *vs.* $[C_{12}mim]Br$ molality exhibit three linear regions.

The apparent molar conductivity of $[C_{12}mim]Br$, Λ, in aqueous electrolyte solutions can be defined as

$$\Lambda = \frac{\kappa - \kappa_0}{m_{IL}} \tag{6}$$

Figure 3b compares the apparent molar conductivity of $[C_{12}mim]Br$ in pure water with those in aqueous solutions of 0.035 mol kg^{-1} different electrolytes at 298.15 K. This figure shows that the values of both $\kappa - \kappa_0$ and Λ in pure water are larger than those in aqueous electrolyte solutions. The apparent molar conductivity of $[C_{12}mim]Br$ in pure water is

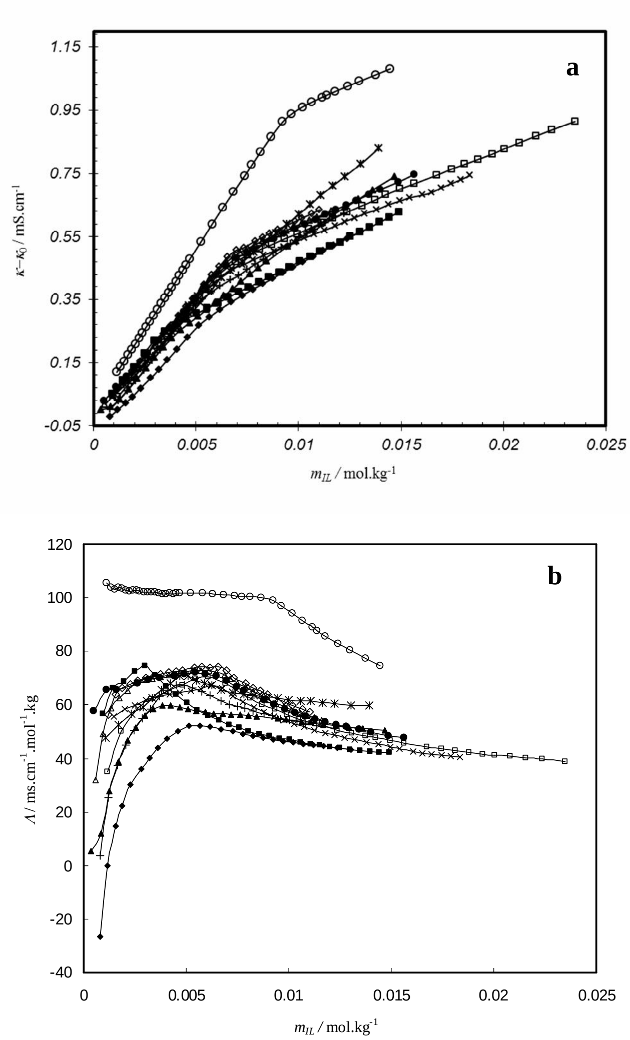

Fig. 3. Plot of $\kappa-\kappa_0$ (a) and Λ (b) against molality of [C$_{12}$mim]Br, m_{IL}, for [C$_{12}$mim]Br in water and in aqueous solutions of 0.035 mol kg^{-1} electrolytes at 298.15 K: ○, pure water; △, NaCl; □, KCl; ◇, NH$_4$Cl; ×, (CH$_3$)$_4$NCl; ■, NaNO$_3$; ●, MgCl$_2$; ◆, Na$_2$CO$_3$; +, Na$_2$SO$_4$; ▲, Na$_3$Cit; *, FeCl$_3$.

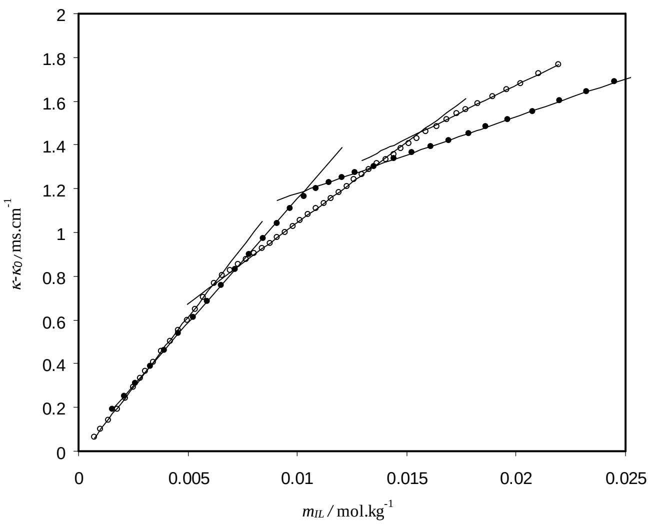

Fig. 4. Plot of $\kappa-\kappa_0$ against molality of [C$_{12}$mim]Br, m_{IL}, for [C$_{12}$mim]Br in water and in aqueous solutions of 0.035 mol kg^{-1} NH$_4$Cl at 308.15 K: ●, pure water; ○, NH$_4$Cl.

almost independent of concentration up to the CAC, and at concentrations higher than the CAC, the value of the apparent molar conductivity decreases as a result of the micelle formation, until a constant value is reached. However, in the presence of electrolytes, the addition of [C$_{12}$mim]Br leads to a sharp increase of Λ at very low concentration and then the values of positive slopes of plots decrease up to the CAC and at concentrations higher than the CAC, the value of the apparent molar conductivity decreases.

The ratio of the slopes of the linear fragments of the specific conductivity isotherms corresponding to the post- and pre-CAC molality ranges was taken as the degree of ionization of the micelles. Therefore, the degree of counter ion binding, β, can be obtained by the relation [40].

$$\beta = 1 - \frac{post\ CAC\ slope}{pre\ CAC\ slope} \tag{7}$$

These values along with the CAC data obtained from the solving of the two linear equations below and above the inflection, observed in the specific conductivity isotherms, are given in Table 1. Temperature dependencies of calculated β values for the investigated systems show that in most cases β decreases with temperature. This behavior indicates that micelles of smaller aggregation number are formed at higher temperatures. In fact the larger micelle has a greater tendency to attract counter ions than the smaller one, which means it has the stronger ability of counter ion binding to micelles, *i.e.*, the larger β value [41]. In this table, the literature values for CMC of [C$_{12}$mim]Br in pure water

Table 1. The Values of β and CAC for [C_{12}mim]Br in Water and in Aqueous Salt Solutions at Different Temperatures

T = 298.15 K		T = 303.15 K		T = 308.15 K		T = 313.15 K	
β	CAC (mmol kg^{-1})	β	CAC (mmol kg^{-1})	β	CAC (mmol kg^{-1})	β	CAC (mmol kg^{-1})
[C_{12}mim]Br in water							
0.730	9.328 [34] 12.0,[34], 9.0,[16]9.53 [13] 10.9,[11] 10.9,[22]9.80, [35] 9.68[23]10,	0.711	9.679	0.694	10.292	0.683	9.962
[C_{12}mim]Br in aqueous solutions of 0.035 mol kg^{-1} NaCl							
0.642	6.737	0.651	6.639	0.558	7.223	0.545	6.545
[C_{12}mim]Br in aqueous solutions of 0.035 mol kg^{-1} KCl							
0.646	6.603	0.631	6.573	0.552	6.892	0.538	6.313
[C_{12}mim]Br in aqueous solutions of 0.035 mol kg^{-1} NH_4Cl							
0.604	6.787	0.620	6.351	0.427	6.165	0.582	6.090
[C_{12}mim]Br in aqueous solutions of 0.035 mol kg^{-1} $(CH_3)_4NCl$							
0.608	6.832	0.601	6.418	0.581	7.072	0.587	6.926
[C_{12}mim]Br in aqueous solutions of 0.035 mol kg^{-1} $NaNO_3$							
0.595	3.294	0.583	3.187	0.514	3.482	0.516	3.466
[C_{12}mim]Br in aqueous solutions of 0.035 mol kg^{-1} $MgCl_2$							
0.586	6.528	0.566	6.103	0.449	7.655	0.452	6.208
[C_{12}mim]Br in aqueous solutions of 0.035 mol kg^{-1} Na_2CO_3							
0.462	5.538	0.341	6.274	0.331	5.441	0.566	5.774
[C_{12}mim]Br in aqueous solutions of 0.035 mol kg^{-1} Na_2SO_4							
0.509	4.985	0.461	5.057	0.417	5.934	0.473	6.305
[C_{12}mim]Br in aqueous solutions of 0.035 mol kg^{-1} Na_3Cit							
0.295	4.035	0.249	4.472	0.367	5.793	0.332	4.520
[C_{12}mim]Br in aqueous solutions of 0.035 mol kg^{-1} $FeCl_3$							
0.375	4.974	0.228	5.160	0.198	5.308	0.347	4.537

are also given at 298.15 K. As can be seen, the obtained value in this work is in a good agreement with those reported in the literature. Furthermore, the obtained value of β for solution of [C_{12}mim]Br in pure water at 298.15 K (0.730) is in a good agreement with those reported in the literature (0.73 [11], 0.78 [34], 0.76 [35], 0.73 [22], 0.76 [16], 0.78 [23]).

Salt Effect on the Thermodynamic Properties and CAC in Aqueous [C_{12}mim]Br Solutions

All the investigated electrolytes effectively reduce CAC of [C_{12}mim]Br in aqueous solutions and therefore they have salting-out effects on the aggregation of [C_{12}mim]Br in aqueous solutions. The results show that the salting-out-inducing anions are predominately responsible for the observed effect, while the cations have a measurable, but smaller effect on the salting-out strength. The observed CAC forming efficiency order of the anions in relation to [C_{12}mim]Br was $NO_3^- \gg Cit^{3-} \gg SO_4^{2-} \approx CO_3^{2-} \gg Cl^-$. The similar trend has also been obtained for conventional cationic surfactants such as [C_{10}mim]Br [36] and alkyltrimethylammonium bromide [42-43]. As can be seen, $FeCl_3$ has a strong salting-out effect on the aggregation of [C_{12}mim]Br, but Wang *et al.* [36] found that $FeBr_3$ and $AlBr_3$ have salting-in effect on the aggregation of [C_{10}mim][Br]. Freire *et al.* [44] found that, an IL salting-in region (the increase of solubility of IL in water in the presence of electrolyte) is observed at low electrolyte concentrations with the electrolytes NaCl, LiCl, KCl, $MgCl_2$, $SrCl_2$, $CaCl_2$, $NaCH_3CO_2$, $NaHCO_3$, $NaHSO_4$, Na_2CO_3 and $Na_3C_6H_5O_7$, followed by salting-out at higher electrolyte concentrations. At an electrolyte concentration of 1.5 mol kg^{-1}, the anion and cation efficiencies order for IL solubility were $Sr^{2+} > Ca^{2+} > Mg^{2+} > Na^+ > Li^+ \approx K^+$ and $C_6H_5O_7^{3-} > CO_3^{2-} > SO_4^{2-} > H_2PO^{4-} > CH_3CO_2^- \approx HSO_4^- > Cl^-$, respectively. It was also found that the electrolytes HCl, NH_4Cl, $(CH_3)_4NCl$, NaOH, NaSCN and $NaNO_3$ promote an increasing salting-in of the IL in water following the cation increasing order effect: $NH_4^+ < H^+ < (CH_3)_4N^+$ and the anion increasing order effect: $NO_3^- < OH^- < SCN^-$. The linear relationship has been obtained between the CAC of the surfactant and the effective hydrodynamics radius (R_h) of the counter ion of the added electrolytes [36-42] so that, larger the hydrated ion, weaker is its close approach to the surfactant ions to augment their self-aggregation. As can be seen from Table 1, among all the investigated chloride electrolytes, the strongest salting-out-inducing cation is Fe^{3+} and other singly charged cations have an almost similar behavior. The electrostatic binding of the anions of the added electrolytes with the cationic head groups of [C_{12}mim]Br leads to the reducing the electrostatic repulsion among the [C_{12}mim]Br head groups and then the lowering its CAC value. In the same electrolyte molality, the number of moles of Cl^- in $FeCl_3$ are more than those in the other investigated chloride electrolytes and therefore $FeCl_3$ is more efficient to promote the aggregation of [C_{12}mim]Br than the other chloride electrolytes. The values of R_h of the investigated anions follow the order $SO_4^{2-} > CO_3^{2-} > Cl^- > NO_3^-$, although the salting-out strength of the investigated anions follows the order $NO_3^- \gg Cit^{3-} \gg SO_4^{2-} \approx CO_3^{2-} \gg Cl^-$. The values of degree of counter ion binding, β, for the investigated anions decrease in the order: pure water > $Cl^- > NO_3^- > SO_4^{2-} > CO_3^{2-} > Cit^{3-}$, which is not exactly in our expectation since the stronger anionic bonding results in the more decrease of the CAC. Although calculation of the degree of counter-ion association is problematic and it has been well discussed in details by Galgano and El Seoud [45], if the obtained β is a correct criterion of counter ion binding on the aggregate surface and also if we accept the above explanation for the effect of electrolyte on the CAC, we can expect that the order of β values should be reverse to that of CAC (order of CAC values: $NO_3^- < Cit^{3-} < SO_4^{2-} < CO_3^{2-} < Cl^-$ < pure water) in the presence of different electrolytes. That is to say the CAC lowering by addition of electrolytes to aqueous surfactant solutions has also been observed in the case of nonionic surfactants [46]. Therefore, we may conclude that the screening effect is not the only factor governing the observed salting-out effects. Because of the significant polarization of the dissolved ions, the water structure is greatly changed by the ionic field of the added ions. The reduced ordering (by the ionic field of the added ions) of the water molecules of hydrophobic hydration around the alkyl chain of the non-associated surfactant molecule leads to a decrease in the energy needed for breaking down this structure during the micellization and to a decrease in the endothermic contribution to the value of enthalpy of micellization. On the other hand, the added ions strongly polarize the surrounding water molecules of hydrophilic hydration and lower their free energy, which causes the removal of water from the surfactant hydrophilic hydration shell where the water is in a high-free-energy state. Therefore, these ion-specific hydration effects indirectly weaken the SAIL-water interactions and an effective $[C_{12}mim]^+$-$[C_{12}mim]^+$ interaction is increased which results in a decrease in the solubility of $[C_{12}mim]Br$ in water. By increasing $[C_{12}mim]Br$ concentration and reducing the amount of water for hydration, $[C_{12}mim]Br$ ions are forced by electrolytes as well as their dual nature to form aggregates which promote a salting-out effect and lowering its CAC value. As mentioned above, increasing the chemical potential of water upon micellization indicate that the solute-water interactions in the supposed monomer solutions are stronger than those in the corresponding real micellar solutions, which support our idea that in monomer solutions, the electrolytes and SAIL ions exclude themselves from the vicinity of each other due to their preferential hydration. As can be seen from Fig. 2a, the values of ΔG_w^{mic} $(= x_w(\mu_w^{mic} - \mu_w^{mon}))$ for the investigated electrolytes, which is manifested the increase in chemical potential of water upon aggregation ($\mu_w^{mic} - \mu_w^{mon}$) in the aqueous electrolyte solutions, follow the order: pure water < Cl^- < CO_3^{2-} < NO_3^- < Cit^{3-} < SO_4^{2-} for anions and pure water < $(CH_3)_4N^+$ < Na^+ < K^+ < Mg^{2+} < Fe^{3+} < NH_4^+ for cations. That is to say, in this case, both of cations and anions have roles in the salting-out of SAIL and the ions with higher valence are more effective than ions with lower valence in salting-out the SAILs because of competition for water. Therefore, if the monomers of the SAIL are salted-out by an electrolyte, aggregation is thermodynamically favored and the CAC is reduced. However, if the monomers are salted-in it is expected that the reverse takes place. In addition to a) electrostatic screening and b) ion-specific hydration effects, the competitive counter ion condensation may also be the another factor that affects the salt effect in aqueous SAIL solutions. Addition of a different ion than the counter ion from the surfactant (say X^- ion added to $[C_{12}mim]Br$ solution) would provide a competitive counter ion condensation between Br^- and X^- ions; replacement of the former by the latter is called competitive specific ion effect arising from a partitioning phenomenon [42]. Furthermore, the ion exchange between the anions added and the surfactant counter ion (Br^-) leads to the formation of mixed micelles, whose aggregation numbers, geometry, and degree of counter-ion association are different from those of the parent SAIL and, therefore, this may be another reason for the unexpected effects of the anions on the values of CAC.

CONCLUSIONS

The behavior of vapor-liquid equilibria at 308.15 K and conductometric properties at 298.15, 303.15, 308.15 and 313.15 K of $[C_{12}mim]Br$ aqueous solutions were studied in the absence and presence of a large series of salts KCl, NH_4Cl, $(CH_3)_4NCl$, $MgCl_2$, $FeCl_3$, NaCl, $NaNO_3$, Na_2CO_3, Na_2SO_4 and Na_3Cit. The obtained values for the critical aggregation concentration (CAC) and degree of anions binding at the aggregates surfaces (β) show that all the investigated salts trigger salting-out effects on the aggregation of $[C_{12}mim]Br$ in aqueous solutions, leading to significant downward shifts of both the CAC and β. The ability of the investigated anions to promote the $[C_{12}mim]Br$ aggregation was found to decrease in the sequence NO_3^- >> Cit^{3-} >> SO_4^{2-} ≈ CO_3^{2-} >> Cl^-. However, the values of degree of counter ion binding, β, for the investigated anions decrease in the order: pure water > Cl^- > NO_3^- > SO_4^{2-} > CO_3^{2-} > Cit^{3-}, which is not exactly in our expectation in which the stronger anionic bonding (larger values of β) decreases the electrostatic repulsion between the ionic head group of the $[C_{12}mim]Br$, thus promoting the $[C_{12}mim]Br$ aggregation and lowering the CAC value. It has been proposed that the aggregation behavior of $[C_{12}mim]Br$ in aqueous salt solutions is controlled by the net result of competition between the three factors: a) the progressive screening by anions of the electrostatic repulsion between cationic head groups of the $[C_{12}mim]Br$, b) the competitive counter ion condensation between Br^- and anions of added salts, c) the effects of the ionic field of the added ions on the water molecules of both hydrophilic and hydrophobic hydration of $[C_{12}mim]Br$.

REFERENCES

[1] J.S. Wilkes, Green Chem. 4 (2002) 73.

[2] X. Wang, J. Liu, L. Yu, J. Jiao, R. Wang, L. Sun, J. Colloid Interface Sci. 391 (2013) 103.

[3] J. Luczak, J. Hupka, J. Thoming, C. Jungnickel, Colloids Surf. A 329 (2008) 125.

[4] J. Bowers, C.P. Butts, P.J. Martin, M.C. Vergara-Gutierrez, Langmuir 20 (2004) 2191.

[5] Z. Miskolczy, K. Sebok-Nagy, L. Biczok, S. Gokturk, Chem. Phys. Lett. 400 (2004) 296.

[6] J. Sirieix-Plenet, L. Gaillon, P. Letellier, Talanta 63 (2004) 979.

[7] G. Bai, A. Lopes, M. Bastos, J. Chem. Thermodyn. 40 (2008) 1509.

[8] Q.Q. Baltazar, J. Chandawalla, K. Sawyer, J.L. Anderson, Colloids Surf. A 302 (2007) 150.

[9] M. Blesic, A. Lopes, E. Melo, Z. Petrovski, N.V. Plechkova, J.N.C. Lopes, K.R. Seddon, L.P.N. Rebelo, J. Phys. Chem. B 112 (2008) 8645.

[10] M. Blesic, M.H. Marques, N.V. Plechkova, K.R. Seddon, L.P.N. Rebelo, A. Lopes, Green Chem. 9 (2007) 481.

[11] B. Dong, N. Li, L. Zheng, L. Yu, T. Inoue, Langmuir 23 (2007) 4178.

[12] B. Dong, J. Zhang, L.Q. Zheng, S.Q. Wang, X.W. Li, T.R. Inoue, J. Colloid Interface Sci. 319 (2008) 338.

[13] B. Dong, X.Y. Zhao, L.Q. Zheng, J. Zhang, N. Li, T. Inoue, Colloids Surf. A 317 (2008) 666.

[14] O.A. El Seoud, P.A.R. Pires, T. Abdel-Moghny, E.L. Bastos, J. Colloid Interface Sci. 313 (2007) 296.

[15] I. Goodchild, L. Collier, S.L. Millar, I. Prokes, J.C.D. Lord, C.P. Butts, J. Bowers, J.R.P. Webster, R.K. Heenan, J. Colloid Interface Sci. 307 (2007) 455.

[16] T. Inoue, H. Ebina, B. Dong, L. Zheng, J. Colloid Interface Sci. 314 (2007) 236.

[17] C. Jungnickel, J. Luczak, J. Ranke, J.F. Fernandez, A. Muller, J. Thoming, Colloids Surf. A 316 (2008) 278.

[18] A. Modaressi, H. Sifaoui, M. Mielcarz, U. Domanska, M. Rogalski, Colloids Surf. A 302 (2007) 181.

[19] T. Singh, A. Kumar, J. Phys. Chem. B 111 (2007) 7843.

[20] T. Singh, A. Kumar, Colloids Surf. A 318 (2008) 263.

[21] S.L.I. Toh, J. McFarlane, C. Tsouris, D.W. DePaoli, H. Luo, S. Dai, Solvent Extr. Ion Exc. 24 (2006) 33.

[22] R. Vanyur, L. Biczok, Z. Miskolczy, Colloids Surf. A 299 (2007) 256.

[23] J.J. Wang, H.Y. Wang, S.L. Zhang, H.H. Zhang, Y. Zhao, J. Phys. Chem. B 111 (2007) 6181.

[24] Y. Zhao, S.J. Gao, J.J. Wang, J.M. Tang, J. Phys. Chem. B 112 (2008) 2031.

[25] K.S. Rao, T. Singh, T.J. Trivedi, A. Kumar, J. Phys. Chem. B 115 (2011) 13847.

[26] A. Heintz, J.K. Lehmann, S.A. Kozlova, E.V. Balantseva, A.B. Bazyleva, D. Ondo, Fluid Phase Equilib. 294 (2010) 187.

[27] J. Wang, L. Zhang, H. Wang, C. Wu, J. Phys. Chem. B 115 (2011) 4955.

[28] T. Singh, K.S. Rao, A. Kumar, J. Phys. Chem. B 116 (2012) 1612.

[29] V. Pino, C. Yao, J.L. Anderson, J. Colloid Interface Sci. 333 (2009) 548.

[30] M. Ao, P. Huang, G. Xu, X. Yang, Y. Wang, Colloid Polym. Sci. 287 (2009) 395.

[31] P.D. Galgano, O.A. El Seoud, J. Colloid Interface Sci. 345 (2010) 1.

[32] H. Sifaoui, K. Lugowska, U. domanska, A. Modaressi, M. Rogalski, J. Colloid Interface Sci. 314 (2007) 643.

[33] N.A. Smirnova, E.A. Safonova, Russ. J. Phys. Chem. A 84 (2010) 1695.

[34] Q. Feng, H. Wang, S. Zhang, J. Wang, Colloids Surf. A 367 (2010) 7.

[35] F. Geng, J. Liu, L. Zheng, L. Yu, Z. Li, G. Li, C. Tung, J. Chem. Eng. Data 55 (2009) 147.

[36] H. Wang, Q. Feng, J. Wang, H. Zhang, J. Phys. Chem. B 114 (2010) 1380.

[37] R. Sadeghi, Y. Shahebrahimi, J. Chem. Eng. Data 56 (2011) 789.

[38] E.C.W. Clarke, D.N. Glew, J. Phys. Chem. Ref. Data 14 (1985) 489.

[39] P.C. Shanks, E.I. Franses, J. Phys. Chem. 96 (1992) 1794.

[40] M. Benrraou, B.L. Bales, R. Zana, J. Phys. Chem. B 107 (2003) 13432.

[41] H.K. Tsao, J. Phys. Chem. B 102 (1998) 10243.

[42] K. Maiti, D. Mitra, S. Guha, S.P. Moulik, J. Mol. Liq. 146 (2009) 44.

[43] J.W. Larsen, L.J. Magidl, J. Am. Chem. Soc. 96 (1974) 5774.

[44] M.G. Freire, P.J. Carvalho, A.M.S. Silva, L.M.N.B.F. Santos, L.P.N. Rebelo, I.M. Marrucho, J.A.P. Coutinho, J. Phys. Chem. B 113 (2009) 202.

[45] P.D. Galgano, O.A. El Seoud, J. Colloid Interface Sci. 361 (2011) 186.

[46] P. Mukerjee, C.C. Chan, Langmuir 18 (2002) 5375.