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Study of salt effects on the aggregation behavior of ionic liquid 1-dodecyl-3-methylimidazolium bromide in aqueous solution

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ABSTRACT

The effect of organic electrolytes Me_4NBr, Et_4NBr, Pr_4NBr, Bu_4NBr, Me_4NCl and Me_4NI on the aggregation behavior and thermodynamic properties of surface active ionic liquid (SAIL) 1-dodecyl-3-methylimidazolium bromide ($[C_{12}mim]Br$) in aqueous solution was studied by volumetric, compressibility and conductometric measurements at different temperatures. The results show that all the electrolytes investigated effectively reduce critical micelle concentration and therefore have a salting-out effect on the aggregation of $[C_{12}mim]Br$ in aqueous solutions. It was also found that the salting-out-inducing anions are predominately responsible for the observed effect, while the cations have a very smaller effect on the salting-out strength. The ability of the anions to promote the aggregation of SAIL decreases in the order of $I^- > Br^- > Cl^-$; however all the investigated cations Me_4N^+, Et_4N^+, Pr_4N^+ and Bu_4N^+ have a similar salting-out strength. Changes in the apparent molar volumes and isentropic compressibilities upon micellization were derived and the infinite dilution apparent molar properties of the monomer form of $[C_{12}mim]Br$ were determined. Furthermore the effect of electrolyte on the degree of anionic binding and the thermodynamic parameters of aggregation for $[C_{12}mim]Br$ in aqueous solutions were determined.

1. Introduction

The self-organization of amphiphilic compounds into micelles, vesicles, lamellar structures and membranes plays a crucial role in the efficiency of many chemical and biotechnological processes. The thermodynamic behavior of surface active compounds provides detailed understanding of the micellization phenomenon. Any study of the micellization processes requires complete thermodynamic characterization [1]. Ionic liquids (ILs), which are organic electrolytes having a melting temperature below 373.15 K, bearing long alkyl chains are found to have obvious amphiphilic characters and are named surface active ionic liquids (SAILs), one kind of functional ILs with combined properties of ILs and surfactants [2]. The aggregation behavior of SAILs may influence their potential applications such as synthesis of nanostructured materials in SAILs, chromatographic application of SAILs, and environmental pollution control by SAILs [3,4]. Hence, the aggregation behavior of SAILs as a novel class of surfactants in aqueous solutions has aroused much interest for the understanding of how SAILs participate in practical applications as a component and has been a focus of recent investigations [2,5–32].

The aggregation behavior of surfactants in aqueous solutions can be altered by varying the solution temperature and/or modifying the aqueous solvent quality. The addition of electrolytes, such as simple salts, is a common method for altering the solvent properties of water. The aggregational properties of ionic surfactants in aqueous solutions are very sensitive to the addition of such cosolutes. Electrolytes normally reduce the electrostatic repulsion among the surfactant head groups and therefore decrease the critical aggregation concentration (CAC) of ionic surfactants (salting-out effect). Although the effects of electrolytes on the aggregation behaviors of SAILs in aqueous solutions are vital to many applications for detergency and emulsification in industry, however, very limited information has been reported in the literature in this respect. Furthermore, although downward shifts of the CAC of SAILs by adding electrolytes are documented, however the mechanism of salt effect at molecular level remains unclear. Rebelo et al. [11] found that the electrolytes NaCl, Na_2SO_4 and tetrabutylammonium bromide had salting-out effects on the CAC values of $[C_{10}mim]Cl$ and $[C_{12}mim]Cl$ in aqueous solutions and the CAC values decreased with increasing ionic strength of the added electrolytes. Dong et al. [12] also found that the CAC values of $[C_{10}mim]Br$, $[C_{12}mim]Br$ and $[C_{12}mim][BF_4]$ in aqueous solutions decreased in the presence of the electrolytes NaCl, NaBr and NaI and the effect of anions in the salting-out effect of the investigated SAILs decreased in the order $I^- > Br^- > Cl^-$. Wang et al. [33] investigated the influence of a series of 15 electrolytes 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 electrolytes $FeBr_3$ and $AlBr_3$ have salting-in effect, whereas other investigated sodium electrolytes have salting-out effect

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on the aggregation of [C_{10}mim]Br in aqueous solutions and the ability of the anions to promote aggregation of [C_{10}mim]Br was found to increase in the order: $SCN^- > I^- > C_6H_5COO^- > ClO_3^- > NO_3^- \approx C_4H_4O_6^{2-} > C_6H_5O_7^{3-} > Br^- > SO_4^{2-} > CO_3^{2-} > Cl^- > BrO_3^- > CH_3COO^-$. Recently, Yu et al. [34] studied the effect of three inorganic electrolytes LiCl, NaCl and $MgCl_2$ and four organic electrolytes Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr on the aggregation behavior of the SAIL 1-butyl-3-methylimidazolium dodecylsulfate ([C_4mim][$C_{12}SO_4$]) in the aqueous solution by surface tension, steady-state fluorescence quenching and dynamic light scattering measurements at 25 °C. It was found that all the electrolytes investigated have a salting-out effect, which promotes aggregate formation of [C_4mim][$C_{12}SO_4$].

In this work, the systematic studies on the volumetric, compressibility, and conductometric properties of the aqueous solutions of model SAIL [C_{12}mim]Br are performed in the presence of a large series of organic electrolytes in order to obtain further evidence about the salting effect produced by the addition of different electrolytes to the aqueous solutions of SAILs and make a thorough analysis of the salting-out effects of anions and cations as well as the role of hydrophobic properties of the electrolytes on the aggregation behavior of a SAIL, [C_{12}mim]Br, in an aqueous medium. For this purpose, 4 bromide electrolytes (Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr) and 3 tetramethyl ammonium electrolytes (Me_4NCl, Me_4NBr and Me_4NI) were used in order to individualize the effect of the anion and the cation.

2. Experimental

2.1. Chemicals

Me_4NBr, Et_4NBr, Pr_4NBr, Bu_4NBr, Me_4NCl and Me_4NI were purchased from Merck and were used without further purification. [C_{12}mim]Br with stated purity higher than 98% mass fraction was purchased from Iolitec GmbH. Prior to use, the SAIL was dried under reduced pressure 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.

2.2. Electrical conductivities

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 volume of solvent (electrolyte aqueous solutions) taken in the container. The uncertainty in the measurement of conductivity was estimated to be 0.1%.

2.3. Volumetric and compressibility

The density and sound velocity of the investigated systems were measured at different temperatures by a digital vibrating-tube analyzer (Anton Paar DSA 5000, Austria) with a proportional temperature control that kept the samples at a working temperature within $\pm 10^{-3}$ K. The calibration of the apparatus was carried out with double distilled water, and dry air at atmospheric pressure according to the instrument maker. Densities and ultrasonic velocities can be measured to $\pm 10^{-3}$ kg m^{-3} and $\pm 10^{-2}$ m s^{-1}, respectively, under the most favorable conditions. The experimental uncertainty of density and sound velocity measurements were $\pm 3 \times 10^{-3}$ kg m^{-3} and $\pm 10^{-1}$ m s^{-1}, respectively. The apparent molar volume, V_ϕ, and apparent molar isentropic compressibility, K_ϕ, of [C_{12}mim]Br were computed from the density and sound velocity experimental data according to the following equations:

$$V_\varphi = \frac{1000}{m_{IL} d d_0}(d_0 - d) + \frac{M_{IL}}{d} \quad (1)$$

$$K_\phi = -\left(\frac{\partial V_\phi}{\partial P}\right)_s = \frac{1000(\kappa_s d_0 - \kappa_{s0} d)}{m_{IL} d d_0} + \frac{M_{IL}\kappa_s}{d} \quad (2)$$

where κ_{s0} and κ_s are isentropic compressibilities of solvent and solution, respectively. The isentropic compressibility is defined as:

$$\kappa_s = \frac{1}{d u^2} \quad (3)$$

In the above equations, M_{IL} is the molecular mass of the [C_{12}mim]Br, m_{IL} is its molality, d_0 and d are the densities of the solvent and the solution, respectively and u_0 and u are the sound velocities of the solvent and the solution, respectively. For the systems, containing both electrolyte and [C_{12}mim]Br, the water + electrolyte is considered as the solvent.

3. Results and discussion

In this work, two sets of experiments with more than 1800 different measured data were carried out in order to achieve further understanding about the salting effect produced by the addition of different electrolytes to the aqueous solutions of SAILs. Toward this goal, 4 bromide electrolytes (Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr) and 3 tetramethylammonium electrolytes (Me_4NCl, Me_4NBr and Me_4NI) were selected in order to individualize the effect of the anion and the cation and the electrical conductivity measurements at 298.15, 303.15, 308.15 and 313.15 K and density and sound velocity measurements at 288.15, 293.15, 298.15, 303.15, 308.15 and 313.15 K were carried out for the aqueous solutions of [C_{12}mim]Br in the presence of 0.035 mol kg^{-1} investigated electrolytes.

3.1. Conductometric properties

Fig. 1 illustrates the specific conductivity curves of the [C_{12}mim]Br aqueous solution with and without organic electrolytes (0.035 mol kg^{-1}) at 298.15 K. The similar behavior was obtained for other temperatures.

It is observed that the specific conductivity values fit into two straight lines of different positive slopes and from the location of the abrupt change of slopes, the corresponding value was derived for the CAC. 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 [35]. In the presence of electrolytes, because of the electrolyte–SAIL interaction, the values of $\kappa - \kappa_0$; κ_0 is the specific conductivities of solvent (pure water or 0.035 mol kg^{-1} aqueous electrolyte solutions); decrease. Although the size of cation has not a distinct effect on the values of $\kappa - \kappa_0$, however above the CAC the values of $\kappa - \kappa_0$ decrease by increasing the size of anion of electrolyte.

Close examination of the experimental specific conductivity data in the presence of electrolytes shows that in the [C_{12}mim]Br concentration range smaller than CAC, the plots of $\kappa - \kappa_0$ against m_{IL} show two regions. At very low SAIL molality no increase of the electrical conductivity is observed upon addition of [C_{12}mim]Br. Such solution electrical behavior can be justified by the formation of larger charged species and/or by the charge collapse of ionic species [36] which are in agreement

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