

Electrical conductivity study on micelle formation of long-chain imidazolium ionic liquids in aqueous solution

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Abstract

Electrical conductivity was measured for aqueous solutions of long-chain imidazolium ionic liquids (IL), 1-alkyl-3-methylimidazolium bromides with C₁₂–C₁₆ alkyl chains. The break points appeared in specific conductivity (κ) vs concentration (c) plot indicates that the molecular aggregates, i.e., micelles, are formed in aqueous solutions of these IL species. The critical micelle concentration (cmc) determined from the κ vs c plot is somewhat lower than those for typical cationic surfactants, alkyltrimethylammonium bromides with the same hydrocarbon chain length. The electrical conductivity data were analyzed according to the mixed electrolyte model of micellar solution, and the aggregation number, n , and the degree of counter ion binding, β , were estimated. The n values of the present ILs are somewhat smaller than those reported for alkyltrimethylammonium bromides, which may be attributed to bulkiness of the cationic head group of the IL species. The thermodynamic parameters for micelle formation of the present ILs were estimated using the values of cmc and β as a function of temperature. The contribution of entropy term to the micelle formation is superior to that of enthalpy term below about 30 °C, and it becomes opposite at higher temperature. This coincides with the picture drawn for the micelle formation of conventional ionic surfactants.

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1. Introduction

Ionic liquids (IL) are a class of organic electrolytes which are in molten state around room temperature [1]. Owing to their unique chemical and physical properties, ionic liquids have currently attracted much interest for applications as novel solvents in organic synthesis [1], catalysis [1,2], electrochemistry [3], and liquid/liquid extraction [4–6]. Particularly, they have an advantage as an environmentally benign solvent, i.e., “green solvent,” since their nonvolatile nature can prevent the environmental pollution. Another advantage of ionic liquids is that their physical and chemical properties can be readily adjusted by suitable selection of cation, anion, and substituent.

In recent years, ILs composed of 1-alkyl-3-methylimidazolium cation, C_{*n*}mim⁺, have been extensively studied in the

field of colloid and interface science. Many of them are concerned with the self-assembly of amphiphilic compounds in the ionic liquids. The formation of bilayer membranes from dialkyldimethylammonium bromides in ether-containing ILs was reported by Kimizuka et al. [7]. Anderson et al. [8] have investigated “dry micelles” of some traditional surfactants in two ILs, C₄mim·PF₆ and C₄mim·Cl. A study on lyotropic liquid crystalline phases of an amphiphilic block copolymer, P123, in C₄mim·PF₆ have been reported [9]. Hexagonal liquid crystalline phases formed in ternary systems of Brij97/water/ILs (C₄mim·BF₄ and C₄mim·PF₆) were also investigated [10]. In addition, microemulsions including ILs were studied by a number of research groups, such as Han et al. [11], Eastoe et al. [12], and Zheng et al. [13].

Another category of research works on ILs related to colloid and interface science is the studies which pay attention to the structural resemblance of imidazolium IL with conventional cationic surfactants. Long-chained imidazolium IL must have

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amphiphilic nature considering their chemical structures, and must form various molecular assemblies in “aqueous medium” just as the case of traditional amphiphilic compounds. Then, new application fields would be expected for imidazolium-type ILs in addition to unique solvents. However, the studies belonging to this category are not so many, although several reports are seen concerning the mesophase formation in concentrated aqueous solution [14,15] and the micelle formation in dilute aqueous solution of some imidazolium ILs [16–19].

Previously, we reported a surface chemical study for aqueous solution of long-chain imidazolium ionic liquids, $C_{10}\text{mim}\cdot\text{Br}$, $C_{12}\text{mim}\cdot\text{Br}$, and $C_{12}\text{mim}\cdot\text{BF}_4$ [20]. It was found that the adsorption efficiency and the effectiveness of surface tension reduction derived from the surface tension vs concentration profile were rather higher than those reported for traditional ionic surfactants when compared with the species bearing the same hydrocarbon chain length. The critical micelle concentration (cmc) for the ILs were somewhat lower than those for typical cationic surfactants, alkyl trimethylammonium bromides. These results demonstrate that the surface activity of the imidazolium ILs is somewhat superior to that of conventional ionic surfactants. As an extension of this previous study, we have investigated in the present work the micelle formation of imidazolium ILs with further extended alkyl chains at various temperatures. The micelle formation was followed by electrical conductivity measurements. Quite recently, a similar study on the same IL species at 25 °C has been reported by Biczók et al. [19]. In the present work, the molar conductance data were analyzed applying the mixed electrolyte model of micellar solution developed by Shanks and Franses [21], and the micellar aggregation number and the degree of counterion binding were estimated. Thermodynamic parameters for the micelle formation obtained from the temperature dependence of the cmc and the degree of counterion binding are also reported in this paper.

2. Materials and methods

The ionic liquids examined in the present work are 1-alkyl-3-methylimidazolium bromides, where alkyl groups are dodecyl, tetradecyl, and hexadecyl groups, and they are expressed as $C_{12}\text{mimBr}$, $C_{14}\text{mimBr}$, and $C_{16}\text{mimBr}$, respectively. These imidazolium samples were prepared according to the procedure reported by Dupont et al. [22]. 1-Methylimidazole and excess molar amount of appropriate alkyl bromide were dissolved in dichloromethane, and the mixture was stirred at 75–80 °C for 48 h. The dichloromethane was then removed by the use of rotary evaporator under reduced pressure. The product was purified by recrystallization from ethyl acetate at least four times, and then dried under vacuum for one day. The purity of the product was ascertained by ^1H NMR spectrum in CDCl_3 . The melting temperatures determined by differential scanning calorimetry (DSC) were 45.5 °C ($C_{12}\text{mimBr}$), 55.4 °C ($C_{14}\text{mimBr}$), and 63.1 °C ($C_{16}\text{mimBr}$). Actually, these ILs are not “liquid” at room temperature; however, by definition, the salts whose melting temperature is lower than 100 °C are called ionic liquid. The DSC thermogram obtained for each sample

showed a sharp single endothermic peak corresponding to the melting, which supports the high purity of our samples. Water used for the preparation of the sample solutions was purified by deionization followed by double distillation.

Specific conductivity of the IL solution was measured using a TOA conductivity meter Model CM-40S (Tokyo, Japan) as a function of the IL concentration. The concentration of the sample solution was successively increased by a stepwise addition of 0.10 or 0.20 cm^3 of the concentrated IL solution to 20.0 cm^3 of pure water being initially placed in a cell for conductivity measurements. After each addition, the solution was stirred to ensure the homogeneous mixing, and then was subjected to the conductivity measurement. The conductivity cell was immersed in a water bath, the temperature of which was kept constant within ± 0.1 °C of a desired temperature using a Neslab refrigerated circulation bath RTE-140 (Portsmouth, NH, USA). The conductivity measurements were carried out at five different temperatures for each IL sample, and the measurements were repeated twice at each temperature.

3. Results and discussion

3.1. Concentration dependence of specific conductivity

An example of conductivity measurements is shown in Fig. 1 where the specific conductivity (κ) obtained for $C_{14}\text{mimBr}$ solution is plotted as a function of the IL concentration at various temperatures. The value of κ increases almost linearly with the increase in the $C_{14}\text{mimBr}$ concentration, and the slope changes steeply at certain concentration (denoted by arrow in the figure). This steep change of the slope in κ vs concentration plot demonstrates that the molecular aggregates, or, micelles, start to form at the concentration corresponding to the break point. The critical micelle concentrations (cmc) determined from the break

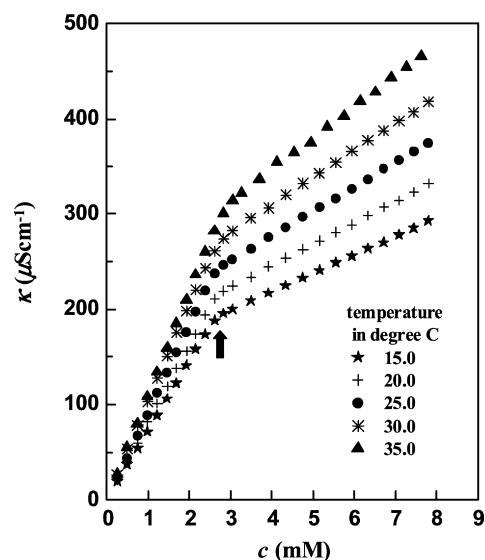


Fig. 1. Plot of specific conductivity, κ , against $C_{14}\text{mimBr}$ concentration, c , at different temperatures. Concentration is in mM where $M = \text{mol dm}^{-3}$. Temperatures are indicated in the figure.

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