

The ionic liquids counterion effect on their aggregation behavior

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Abstract

Surface activity of two kind of ionic liquid-based imidazolium surfactants, "Octadecyl methyl imidazolium tetrafluoroborate" and "Octadecyl methyl imidazolium hexafluorophosphate" was investigated. Critical micelle concentration (cmc) of each ionic liquid was obtained by using empirical methods such as conductometry and tensiometry. The investigations showed that cmc of ODMImPF₆ significantly are less than ODMImBF₄. The results showed that hexafluorophosphate ion can reduce the surface charge of cations due to larger size and more ability in forming hydrogen bonding with water molecules, compared with tetrafluoroborate. In summary, these factors cause the reduction in repulsion forces between head groups and consequently cations can more easily be placed side by side to form micelles. Moreover, cmc of their mixtures is different from that of Clint's relation, because of synergistic effect.

Keywords: Aggregation; Critical micelle concentration; Ionic liquids counterion; Tensiometry; Conductometry; Synergistic effect.

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], and electrochemistry [3]. ILs can act not only as surfactants, but also as a solvent. The unique advantage of ionic liquids as solvents is that their physical and chemical properties can be readily adjusted by suitable selection of cation, anion, and the substituents of cation. Aggregates such as micelles, liquid crystals and microemulsions formed in ILs have been widely studied recently [4].

2. Materials and methods

2.1. Materials

The ODMImBr and ODMImCl ionic liquids were synthesized in our laboratory by the procedure reported in the literature [5].

2.2. Surface Tension Measurements

Surface tension measurements were conducted on a Model KSV sigma 700 tensiometer using the ring method. Surface tension measurements were performed to investigate the aggregation behavior of the long-chain ILs in water. Fig. 1 shows the surface tension (γ) versus concentration (C). Plot obtained for two long-chain ILs and their equal mixture (Fig. 2) in water at 25°C. It is clearly seen that the surface tension of the IL/Water solutions decreased along with the increase of the concentration of the ionic liquids, indicating their adsorption at the air/solution interface. As the concentration is increased further, distinct break points appear which indicate the formation of aggregates. After the break point, the surface tension continued to decrease as the concentration of the ILs increased. The values of the critical micelle concentration (cmc) were determined from the intersection of two straight lines drawn in diagram.

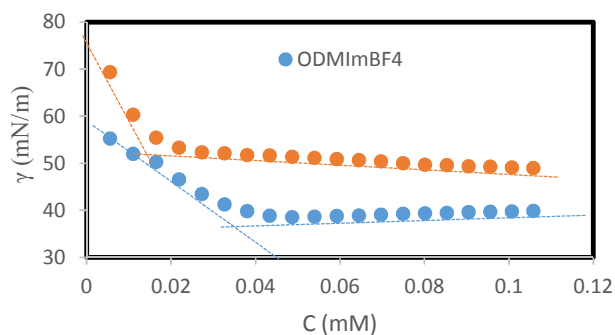


Fig. 1. Surface tension as a function of concentration for ILs in water at 25°C.

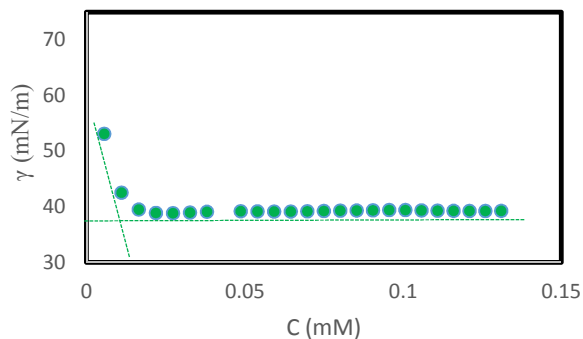


Fig. 2. Surface tension versus concentration of mixed ILs in water at 25°C.

2.3. Conductometry

Electrical conductivity was measured for aqueous solutions of two imidazolium ionic liquids (ILs), 1-octadecyl-3-methylimidazolium with tetrafluoroborate and hexafluorophosphate anions. Conductometric measurements were performed by using JENWAY 4510 conductometer in room temperature. The break points appeared in specific conductivity (k) vs concentration (c) plot indicates that the molecular aggregates, i.e., micelles, are formed in aqueous solutions of IL species. Fig. 3 shows the conductivity (k) versus concentration (C) of ODMImBF₄ and ODMImPF₆.

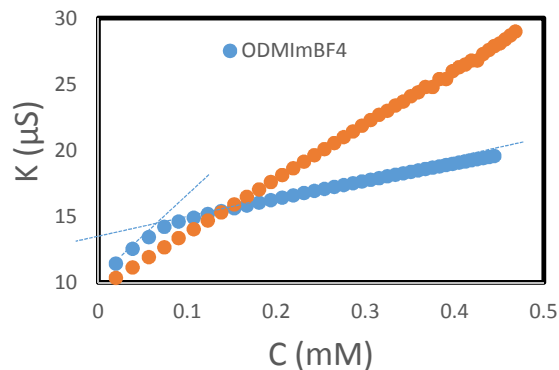


Fig. 3. Plot of conductivity (K) against ODMImBF₄ and ODMImPF₆ concentration (C).

Since the dissociation degree of ODMImPF₆ is much less than that of ODMImBF₄, its break point (cmc) not be measured by conductometry accurately.

Conductometry of mixed ILs was performed at the room temperature and its break point shows that the cmc obtained it, is approximately match with that of tensiometry data.

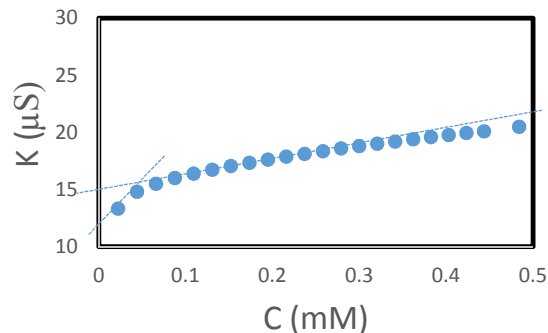


Fig. 4. Conductometry of mixed ILs at room temperature.

Table 1 shows the CMC of two ionic liquids and their equal mixture. According to the table data, the critical concentration of ODMImPF₆ is less than that of ODMImBF₄. Since the cations are similar, the difference in CMCs is due to difference of counterions.

Table 1. Critical micelle concentrations (mM) obtained from different methods

	Tensiometry	Conductometry
ODMImBF ₄	0.04	0.07
ODMImPF ₆	0.02	-
Mixture	<0.02	0.05

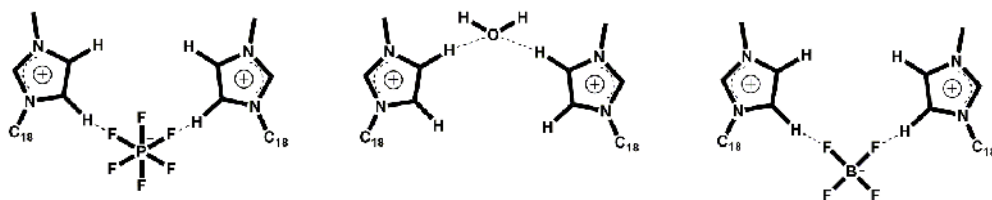
Clint has shown that for an ideal binary surfactant mixture the critical micelle concentration CMC_{12}^{id} can be calculated from single component values, CMC_1 and CMC_2 , and the mole fraction of a component in the mixture, α_1 , as described by Equation 1.

$$\frac{1}{CMC_{12}^{id}} = \frac{\alpha_1}{CMC_1} + \frac{(1-\alpha_1)}{CMC_2} \quad (1)$$

Here in ODMImBF₄ and ODMImPF₆ have been denoted as components 1 and 2, respectively. Since both materials are mixed in equal proportions, mole fraction for both of them is equal to 0.5 and the CMC of mixture will be 0.026 mM, but experimental results showed that is less than 0.02mM.

One of the properties of ionic liquids is ability to establish hydrogen bonds. In the system studied, the anion also has the ability of establish hydrogen bonds with water molecules, because of their fluorine atoms.

This schematic shows that the hydrogen bonds how to be formed in IL/Water system.



Scheme 1. Scheme 1. Schematic showing the hydrogen bonding between water or anions and ODMIm⁺

In fact, the establishment of hydrogen bonds between the ionic liquid molecules causes the formation of a network between them. In result, the system is divided into two phases, the water molecules and ionic liquid which are assembled together by hydrogen bonds. Ability to establish hydrogen bonds between cations, is a driving factor for micelle formation in compare with repulsive forces between head groups.

4. Conclusion

The investigations showed that cmc of ODMImPF₆ are less than ODMImBF₄. The results showed that hexafluorophosphate ion can reduces the surface charge of cations due to larger size and more ability in forming hydrogen bonding with water molecules, compared with tetrafluoroborate. Also, these factors cause the reduction in repulsion forces between head groups and consequently cations can more easily be placed side by side to form micelles. This study could significantly broaden the potential application of mixed micelles in ILs where specific conditions are demanding (e.g., high temperature, low pressure, and broad composition range).

References

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