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Salting out effects on adsorption and micellization of three imidazolium-based ionic liquids at liquid–liquid interface

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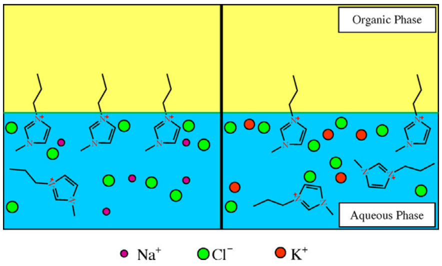
HIGHLIGHTS

- Electrolytes fortify ILs interface activity at toluene–water interface.
- Sodium chloride has stronger effect on ILs adsorption than potassium chloride.
- The experimental data are well fitted with the Frumkin adsorption isotherm.
- Adsorption tendency and effectiveness increase with electrolyte concentration.
- Repulsive interaction of adsorbed molecules decreases with electrolyte concentration.

GRAPHICAL ABSTRACT



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ABSTRACT

The effects of sodium chloride and potassium chloride electrolytes on adsorption and micelle formation of three amphiphilic ionic liquids (ILs), 1-alkyl-3-methylimidazolium chloride, [$C_n$mim][Cl], $n = 6$, 7 and 8, at the toluene-water interface were investigated. Temperature was fixed at 298.2 K. Due to interface activity, the used ILs significantly reduce the interfacial tension and in the order of their alkyl chain length. The presence of electrolytes results in the salting out effects and intensifies reducing the interfacial tension and micelle concentrations of ILs. To fit experimental data, the Frumkin adsorption isotherm was satisfactorily applied below the critical micelle concentrations of the ILs. As a result, the adsorption parameters including adsorption tendency and saturated interface excess rise to higher levels and the electrostatic repulsion between the adsorbed IL molecules declines in the presence of electrolytes; however, the variations are more significant with sodium chloride because of smaller and more hydrated cation.

1. Introduction

Ionic liquids (ILs) are molten salts comprising bulky organic cation and inorganic anions at room temperature [1]. Due to their negligible volatility, non-flammability and high thermal stability [2], they have been considered in many fields ranging from catalyst applications [3] to different separation techniques such as membrane [4] and liquid–liquid extraction [5].

In recent decades, ILs have received much attention in the colloid and interface sciences because of their amphiphilic structures which act as a new class of cationic surfactants [6–8]. The surface properties and micelle formation of ILs in aqueous media have been widely investigated by surface tension measurements [9–11]. These characters can be altered with the alkyl chain length of cationic head group and nature of anions. For instance, Sastry et al. [12] have reported that the surface activity as well as critical micelle concentration (CMC) of imidazolium-based ILs depend

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Nomenclature

b_F	adsorption equilibrium constant ($dm^3\ mol^{-1}$)
C_{IL}	ionic liquid concentration ($mol\ dm^{-3}$)
C^*	activity ($mol\ dm^{-3}$)
$f_\pm$	average activity coefficient
I	ionic strength ($mol\ dm^{-3}$)
OF	objective function
r	the capillary radius (mm)
R	gas law constant ($J\ mol^{-1}\ K^{-1}$)
T	temperature (K)
V	drop volume (mm^3)

Greek symbols

γ	interfacial tension ($mN\ m^{-1}$)
ρ	density ($kg\ m^{-3}$)
Δ	difference
$\varphi(r/\sqrt[3]{V})$	Harkins and Brown constant
Π	interfacial pressure ($mN\ m^{-1}$)
ω	partial molar area ($m^2\ mol^{-1}$)
θ	interface layer coverage
Γ	interface excess concentration ($mol\ m^{-2}$)
β	intermolecular interaction parameter
ε_r	relative permittivity of water
ΔG°_{ads}	standard free energy of adsorption ($kJ\ mol^{-1}$)
ρ'	molar concentration of water ($mol\ dm^{-3}$)
Γ_m	maximum interface excess ($mol\ m^{-2}$)

Subscripts

ads	adsorption
F	Frumkin
m	maximum

on the alkyl chain length of cationic head group. Higher reduction in the surface tension of air–water were relevant with the IL consisting longer alkyl chain. Recently, a series of 1-alkyl-3-methylimidazolium alkyl sulfates, denoted as salt-free ionic liquids, have been synthesized and their surface properties in aqueous solutions examined by surface tension measurements [13]. These sorts of ILs with alkyl-substituted imidazolium cations and alkyl sulfate anions show superior surface activity than the corresponding imidazolium-based ILs with inorganic anions. Moreover, addition of inorganic electrolytes has modified the surface activity of ILs and reduced the CMC values through the salting out effect and decreasing the electrostatic repulsion between charged hydrophilic portions of ILs [14]. Similar researches have revealed that ILs can be used as dispersant [15] and foaming [16] agents in many industries analog to conventional surfactants. Along with these usages, emulsion of ILs is significant in the fields dealing with air pollution. In this respect, oxidative-extractive desulfurization of fuels with emulsions of ILs has been developed to diminish sulfur-containing compounds [17].

Since ILs can tolerate high salinity, there are opportunities to replace surfactants with ILs in many petroleum industries such as enhanced oil recovery (EOR) processes [18]. Nevertheless, few literatures are focused on the interfacial behavior of ILs at oil–water systems [19,20].

The aim of the present study is to investigate the role of sodium chloride and potassium chloride (usually present, to some extent, in water sources) on the adsorption of three imidazolium-based ILs, 1-alkyl-3-methylimidazolium chloride, briefly [C$_n$mim][Cl], $n = 6$, 7 and 8, at the interface of toluene-water system. Accordingly, interfacial tension (IFT) variations are reported and the CMC and related parameters of interfacial activity such as the adsorption tendency, interface excess concentration and interaction parameter between the adsorbed ILs at different electrolyte concentrations are obtained. The experimental data are correlated with the Frumkin adsorption isotherm for the IL concentrations less than the CMCs.

Table 1
Provenance and purity of the used materials.

Chemicals	Provenance	Purity%
Toluene	Merck	99.9
Sodium chloride	Merck	99.5
Potassium chloride	Merck	99.5
1-Methylimidazole	Merck	99
1-Chlorohexane	Merck	99
1-Chloroheptane	Merck	98
1-Chlorooctane	Riedel-de Haen	96
Ethyl acetate	Merck	99.5

2. Experimental

2.1. Materials

The toluene-water system was chosen as a recommended chemical system for liquid–liquid extraction investigations known as a high IFT system [21]. Freshly deionized water, with electrical conductivity of 0.08 $\mu S\ cm^{-1}$, was used for preparing aqueous solutions. Relevant information on the provenance and purity of materials including sodium chloride (NaCl), potassium chloride (KCl), toluene and chemicals for ILs synthesizing are given in Table 1. Each IL was synthesized and purified according to the standard method [22]. The detailed procedure including synthesis and characterization are described in our preceding investigation [23].

2.2. IFT measurements

The IFT measurements were performed using the drop volume method. The drop-forming device and the procedure were similar to that detailed in a previous study [24]. In this method, the IFT (γ) can be expressed by Harkins and Brown equation [25]:

$$\gamma = \frac{V\Delta\rho g}{r}\varphi\left(\frac{r}{\sqrt[3]{V}}\right) \tag{1}$$

where V is drop volume falling off a capillary into the organic phase; $\Delta\rho$ is the density difference between the aqueous and organic liquids (ρ_w and ρ_o), g and r are acceleration of gravity and the capillary radius, respectively, and $\varphi(r/\sqrt[3]{V})$ is a constant which can be obtained from empirical relations [26]. The range of generated drop volumes, drop formation times and $r/\sqrt[3]{V}$ (dimensionless) values for the system containing each IL in the presence of electrolytes are presented in Table 2. The maximum uncertainties for drop volumes, drop formation time and the IFT measurements were determined $\pm 0.1\ mm^3$, ± 0.01 s and $\pm 0.1\ mN\ m^{-1}$, respectively.

To ensure fine performance of the method, the IFT of pure toluene–water system (binary saturated, without IL) was measured and compared with the values reported in the literatures at 298.2 K. The obtained value of 36.3 $mN\ m^{-1}$ was in agreement with the reported values of 36.1 [27] and 36.6 $mN\ m^{-1}$ [28]. Solutions

Table 2
The range of generated drop volumes, V, drop formation times, t, and $r/\sqrt[3]{V}$ values for each IL without and in the presence of electrolytes.

IL	V (mm^3)	t (s)	$r/\sqrt[3]{V}$
[C$_6$mim][Cl]	81.5–272.3	140.36–469.27	0.3471–0.5191
[C$_7$mim][Cl]	64.0–270.3	110.30–465.72	0.3480–0.5625
[C$_8$mim][Cl]	54.1–268.6	93.26–462.79	0.3487–0.5948