Contents lists available at ScienceDirect

## Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

## Alkyl chain length, counter anion and temperature effects on the interfacial activity of imidazolium ionic liquids: Comparison with structurally related surfactants

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#### ARTICLE INFO

ABSTRACT

Article history: Received 14 August 2014 Received in revised form 27 November 2014 Accepted 1 December 2014 Available online 3 December 2014

Keywords: Ionic liquids Surfactants Interfacial tension Frumkin isotherm Szyszkowski equation Adsorption of three long-chain imidazolium ionic liquids (ILs) at toluene–water interface was studied along with their micelle formations at temperatures within (293.2–313.2) K. The used ILs act as excellent surfactants and under the same conditions, their interfacial activity is reasonably appeared in the order of  $[C_{16}mim][Br] > [C_{16}mim][C]] > [C_{12}mim][C]]$ . The experimental data were satisfactorily reproduced by the Frumkin adsorption isotherm for concentrations less than critical micelle concentration (CMC). Accordingly, the highest maximum interface excess and adsorption equilibrium constant were for  $[C_{16}mim][Br]$  because of its long alkyl chain as well as more polarizable anion. In this regard, the balance between electrostatic repulsion and van der Waals attraction provides a stronger attractive interaction for this IL. On the other hand, by rising temperature, the interface excess concentration, adsorption tendency and electrostatic repulsion between adsorbed molecules increase. The results show that, within the same concentration ranges, the maximum interfacial tension reduction were 72% for  $[C_{12}mim][C1]$  and  $[C_{16}mim][Br]$  ILs, compared with 68% for similarly structure DTMAC and CTAB surfactants. Also, these ILs, respectively, have the CMC values about 81% and 63% of related surfactants.

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#### 1. Introduction

In recent decades, ionic liquids (ILs) are greatly concerned by researchers in different fields such as catalyzing [1], electrochemistry [2] and liquid–liquid extraction [3]. Because of high ion conductivity, negligible volatility, non-flammability and high thermal stability, wide range of applications are possible [4]. ILs capabilities can be changed by altering/modifying cations and/or anions [5].

Along with outstanding features, ILs have revealed excellent surfactant properties owing to amphiphilic structure which gives them ability to adsorb at the surface/interface and form micelle [6–8]. For instance, it has been reported that the surface tension and critical micelle concentration (CMC) of different kinds of ILs with long hydrocarbon chain (10–18 carbons) decrease by increasing alkyl chain length [8]. Not only has the alkyl chain length of ILs effect on the adsorption, but also the kind of anion has. Li et al. [9] demonstrated that counter anion of an IL with weaker hydration potential causes a higher surface activity.

Despite the widespread attention to the surface activity, few studies have focused on the interfacial properties of ILs at the oil-water interfaces [7]. It is while there is a great opportunity to utilize ILs to decrease the interfacial tension (IFT) of oil and water in petroleum industries [10].

The present study is conducted in order to investigating the role of alkyl chain length, counter anion and temperature on the adsorption of long-chain imidazolium-based ILs, 1-dodecyl-3methylimidazolium chloride, briefly [C12mim][Cl], 1-hexadecyl-3-methylimidazolium chloride, [C16mim][Cl], and 1-hexadecyl-3methylimidazolium bromide, [C<sub>16</sub>mim][Br], at the interface of toluene-water system. In the field of interest, a precise comparison is provided between ILs and structurally related cationic surfactants, dodecyl trimethyl ammonium chloride, DTMAC, and hexadecyl trimethyl ammonium bromide (cetyl trimethyl ammonium bromide). CTAB. Accordingly, the IFT variations with each IL concentration, at different temperatures, are reported and the influence of carbon numbers in alkyl chain as well as the anion is examined. The data are reproduced by the Frumkin adsorption isotherm for concentrations less than the CMCs of ILs. Accordingly, the maximum interface excess concentration, interaction parameter between the adsorbed ILs and the adsorption tendency at different temperatures are obtained. Finally, the interfacial adsorption parameters of the used surfactants were obtained by





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#### Nomenclature

- a Diameter (Å)
- A Constant in Eq.(2), area occupied by molecules
- b Adsorption equilibrium constant (dm<sup>3</sup> mol<sup>-1</sup>)
- B Constant in Eq.(2)
- C Ionic liquid or surfactant concentration (mol dm<sup>-3</sup>)
- $CMC^*$  Effective critical micelle concentration (mol dm<sup>-3</sup>)
- $f_{\pm}$  Average activity coefficient
- g Acceleration of gravity
- I Ionic strength ( $mol dm^{-3}$ )
- *K* Adsorption equilibrium constant ( $dm^3 mol^{-1}$ )
- *N*<sub>Av</sub> The Avogadro's number
- OF Objective function
- *r* The capillary radius (mm)
- *R* Gas law constant  $(I \mod^{-1} K^{-1})$
- *R*<sup>2</sup> Coefficient of determination
- *T* Temperature (K)
- v Drop volume (cm<sup>3</sup>)
- z Ion charge

Greek symbols

γ	Interfacial tension $(mNm^{-1})$
ρ	Density (kg m <sup>-3</sup> )
$\Delta_{\perp}$	Difference
$\varphi(r/\sqrt[3]{V})$	Harkins and Brown constant
$\Pi'$	Interfacial pressure (mN m <sup>-1</sup> )
$\theta$	Interface layer coverage
Γ	Interface excess concentration (mol m <sup>-2</sup> )
β	Interaction parameter
e <sub>r</sub>	Relative permittivity of water
$\Delta G_{ads}^{\circ}$	Standard free energy of adsorption $(kJ mol^{-1})$
$\rho'$	Molar concentration of water (mol dm <sup>-3</sup> )
Subscripts	
ads Adsorption	
Av Avogadro	
cal Calculated	
exp Experimental	
F Frumkin	
L Langmuir	
m Max	imum, minimum
Superscripts	
* Effective value	

using Szyszkowski equation and compared with those obtained for ILs.

#### 2. Experimental

#### 2.1. Materials

The widely used toluene–water chemical system, with a relatively high IFT, was utilized. Toluene, DTMAC, CTAB (purity in mass fraction more than 0.999, 0.98 and 0.99, respectively) and raw materials for ILs synthesizing, including 1-methylimidazole, 1-dodecylchloride, 1-hexadecylchloride, 1-hexadecylbromide and ethyl acetate with mass fraction purity of 0.99, 0.95, 0.96, 0.96 and 0.995, respectively, were all purchased from Merck and were used without further purification. Aqueous solutions were prepared with newly deionized water having electrical conductivity of 0.07  $\mu S \, cm^{-1}$ .

#### 2.2. Synthesizing and characterization of ILs

Three long-chain imidazolium-based ILs,  $[C_{12}mim][Cl]$ ,  $[C_{16}mim][Cl]$  and  $[C_{16}mim][Br]$ , were prepared according to the previous procedure [11]. Briefly, equal molar amounts of 1-methylimidazole and appropriate 1-alkylhalide were mixed and stirred rigorously in a round-bottomed flask equipped with a reflux condenser for 48 h at 70 °C. Reactions were performed in solvent-free condition, nitrogen atmosphere and also protected from the light. The produced ILs were allowed to cool to room temperature. The waxy solid products were washed with ethyl acetate, at least ten times, to remove any unreacted reagent. After the last washing, the remaining ethyl acetate was removed by heating to 77 °C. As a preliminary estimation, purity of ILs was examined by halide titration and purity more than 99% was found for each of them.

The synthesized ILs were characterized by means of FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectroscopy. Characterization details as well as all the relevant spectra are given in supplementary information.

#### 2.3. IFT measurements

The drop volume method was used for measuring the IFT values. The drop-forming device and the detailed procedure were described in our previous study [12].

Prior to the IFT measurements, solutions containing individual IL or cationic surfactant were prepared in mass with an Ohaus (Adventurer Pro AV 264) balance (uncertainty of  $\pm 0.1$  mg). For preparation of desired solutions, volumetric pipettes (5 and 10 cm<sup>3</sup> with maximum uncertainty of  $\pm 0.02$  cm<sup>3</sup>) and volumetric flasks (200 and 250 cm<sup>3</sup> with uncertainty of  $\pm 0.2$  cm<sup>3</sup>) were used. Ranges of concentration within ( $2.50 \times 10^{-6}$  to  $2.50 \times 10^{-3}$ ) mol dm<sup>-3</sup> for [C<sub>16</sub>mim][Cl], [C<sub>16</sub>mim][Br] and CTAB and ( $1.00 \times 10^{-5}$  to  $7.00 \times 10^{-2}$ ) mol dm<sup>-3</sup> for [C<sub>12</sub>mim][Cl] and DTMAC were chosen. The absolute standard deviation of concentrations does not exceed  $\pm 0.01 \times 10^{-3}$  mol dm<sup>-3</sup>. After solution preparation, equal volumes of aqueous and organic phases (100 cm<sup>3</sup>) were mixed for 1 h, and then left at rest for another hour. It is notable that forming emulsion below the CMCs was not observed.

Both the organic and aqueous phase samples were withdrawn to measure the density by means of an oscillating U-tube densimeter (Anton Paar DMA 4500, Austria), provided with automatic viscosity correction. The uncertainty for density measurements was  $\pm 0.01$  kg m<sup>-3</sup>.

By using a calibrated thermostat (OPTIMA 740, Japan) with an uncertainty of  $\pm 0.1$  K, the measurements of IFT were conducted at different temperatures.

In the drop volume method, IFT,  $\gamma$ , is expressed by Harkins and Brown equation [13]:

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

where *v* is drop volume, falling off a capillary (with *r* radius of 2.25 mm) into the organic phase;  $\Delta \rho$  and *g* are the density difference between the aqueous and organic phases,  $\rho_w$  and  $\rho_o$ , and gravitational acceleration, respectively. The constant  $\varphi(r/\sqrt[3]{v})$  can be extracted from empirical relation proposed by Lee et al. [14]. Experimental parameters such as the phase densities, drop formation time and IFT data are given in Supplementary information for ILs or surfactant at used concentrations and applied temperatures. The range of drop formation time was (75–466)s for [C<sub>12</sub>mim][Cl], (60–452)s for [C<sub>16</sub>mim][Cl] and (60–428)s for [C<sub>16</sub>mim][Br]. Besides, the ranges of (128–450)s and (120–417)s were corresponding to DTMAC and CTAB,

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