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# Adsorption behavior of long alkyl chain imidazolium ionic liquids at the n-butyl acetate + water interface



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#### ARTICLE INFO

#### ABSTRACT

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Keywords: Imidazolium ionic liquids Long alkyl chain n-Butyl acetate–water Interfacial tension Szyszkowski equation The adsorption behavior of amphiphilic long alkyl chain imidazolium ionic liquids (ILs), 1-alkyl-3-methylimidazolium chloride {[ $C_nmim$ ][Cl], n = 12, 14, 16} at the interface of n-butyl acetate + water system was studied. Within IL bulk concentration range of  $1.00 \cdot 10^{-5}$ - $1.00 \cdot 10^{-2}$  mol/dm<sup>3</sup> and temperature of 293.2–318.2 K, the used ILs act as excellent surfactants and reduce the interfacial tension significantly. The corresponding interfacial activity appeared logically in the order of [ $C_{16}$ mim][Cl] > [ $C_{14}$ mim][Cl] > [ $C_{12}$ mim][Cl]. An almost linear decrease in interfacial tension was also relevant by temperature. For modeling, the Szyszkowski adsorption equation was used to reproduce the experimental data. The consistent fittings confirm the ideal adsorption of the used IL molecules at the interface. Results also show that adsorption effectiveness increases with the alkyl chain length; however, it declines with temperature. On the other hand, adsorption tendency increases with alkyl chain length as well as with temperature. Negative standard free energy values indicate simultaneous adsorption for all cases.

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#### 1. Introduction

Ionic liquids (ILs) are a remarkable group of chemicals that have found widespread applications in different areas such as catalyzing reactions [1], corrosion inhibition [2], gas–liquid absorption [3], liquid membrane separation [4], and liquid–liquid extraction [5]. Interests in ILs include their amazing applications and characters with respect to their properties such as non-flammability, high thermal stability, and ion conductivity. The desired properties can be provided in ILs by the alteration in their cation and anion structure [6].

One excellent activity, stemming from amphiphilic nature, is the ILs surface/interface adsorption. ILs possess cationic hydrophilic (head group) and hydrophobic (tail) portions, facilitating their ease of adsorption at the interfaces. Accordingly, interfacial tension (IFT) is frequently considered which reflects the unbalanced forces at the interface [7]. Materials such as surfactants and electrolytes can alter this property due to their adsorption and the extent of variation reflects the nature and the impact level of adsorption. IFT plays an important role in interphase heat and mass transfer particularly in extraction and emulsification processes [8].

In recent years, one of the most widely used ILs is the imidazoliumbased structures that exhibit excellent surface activity [9]. In this regard, the surface and aggregation behavior of aqueous mixtures containing 1alkyl-3-methylimidazolium halides have been studied with a variety of methods [10,11].

Despite a lot of studies on ILs, there is scarce literature on their adsorption at the interfaces. In an attempt, the behavior of ILs at the interface of toluene + water was studied [12]. The work was recently continued on the n-butyl acetate + water system with short alkyl chain imidazolium-based ILs [13]. This chemical system is known as an "intermediate IFT system" and is recommended by the EFCE working party [14] for liquid-liquid extraction studies [15-17]. The used ILs meaningfully reduced the IFT and the adsorption tendency exhibited increasing with temperature. The present study was aimed to identify the function of long alkyl chain imidazolium-based ILs namely, 1-dodecyl-3-methylimidazolium chloride, 1-tetradecyl-3-methylimidazolium chloride, and 1-hexadecyl-3-methylimidazolium chloride {briefly:  $([C_n mim][Cl], n = 12, 14 \text{ and } 16)$  at the n-butyl acetate + water interface. Very low but effective IL concentrations were used here under conventional temperatures. Accordingly, the experimental data were reproduced using a theoretical model and the relevant parameters were obtained.

#### 2. Experimental

#### 2.1. Materials

In this study, n-butyl acetate + water chemical system was used to study the influence of ILs adsorption. N-butyl acetate with mass fraction purity of more than 0.995 was obtained from Merck. The raw materials for synthesizing and purifying ILs, including: 1-methylimidazole, 1dodecylchloride, 1-tetradecylchloride, 1-hexadecylchloride, and ethyl acetate were also purchased from Merck with mass fraction purities

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more than 0.999, 0.95, 0.96, 0.96, and 0.995, respectively. All materials were used without further purification. Fresh deionized water with electrical conductivity of 0.07  $\mu$ S/cm was used as aqueous phase. The specifications of the utilized chemicals are given in Table 1.

#### 2.2. Synthesis and characterization of the ILs

The long chain imidazolium-based ILs, [C<sub>12</sub>mim][Cl], [C<sub>14</sub>mim][Cl], and [C<sub>16</sub>mim][Cl], were synthetized according to the previously reported procedure [18]. In an abbreviated manner, equal molar amounts of 1methylimidazole 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 while protected from the light. The products were allowed to cool to room temperature. The waxy ILs were then washed with ethyl acetate for at least ten times, to remove any unreacted reagents. After the last washing, the remaining ethyl acetate was removed by heating to 77 °C. As a preliminary estimation, the quality of products was tested by halide titration, and purities more than 99% were found. In addition, the synthesized ILs were characterized by means of FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectroscopy. The data of characterization were in agreement with the expected structure. The details of spectra are presented in supplementary data as well as chemical formula, color, and state of the used ILs. To examine the purity, chloride titration was also employed to determine the chloride content of the ILs [19] and purity more than 99% was obtained for each of the ILs.

#### 2.3. IFT measurements

The drop volume method was used for determining the IFT values. It is a reproducible technique, frequently used in the measurements [20–23]. In this method, the IFT,  $\gamma$ , is calculated from Harkins and Brown equation [24]:

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

where *V* is the aqueous drop volume falling off a capillary into the organic phase;  $\Delta \rho$  is the density difference between the aqueous and organic liquids ( $\rho_w$  and  $\rho_o$ ), *g* and *r* are the acceleration of gravity and the capillary radius (0.35 mm in this study), respectively, and  $\phi(r/\sqrt[3]{V})$  is a constant (dimensionless) which can be obtained from empirical relations [21].

Aqueous phase concentrations of ILs, within  $1.00 \cdot 10^{-5}$ – $1.00 \cdot 10^{-2}$  mol/dm<sup>3</sup> were prepared by mass, using an Ohaus (Adventurer Pro, AV 264) balance with an uncertainty of  $\pm 0.1$  mg. In this regard, 200 and 250 cm<sup>3</sup> volumetric flasks with an uncertainty of  $\pm 0.2$  cm<sup>3</sup> and 5 and 10 cm<sup>3</sup> volumetric pipettes with a maximum uncertainty of  $\pm 0.02$  cm<sup>3</sup> were used. Accordingly, the absolute standard deviation of concentrations did not exceed  $\pm 0.01 \cdot 10^{-3}$  mol/dm<sup>3</sup> for all cases. Prior to experiments, equal volumes of aqueous and organic phases (100 cm<sup>3</sup>) were mixed for at least 30 min, and then left to rest for another 30 min. It is notable that the mutual solubility of both the organic and aqueous phases was very low and forming emulsion of either phase in

#### Table 1

Mass fraction purity and CAS number of the used materials (all Merck products).

Chemical name	Mass fraction purity <sup>a</sup>	Water mass fraction	CAS number
n-butyl acetate	>0.995	<0.001	123-86-4
1-Methylimidazole	>0.999		616-47-7
1-Dodecylchloride	>0.95		112-52-7
1-Tetradecylchloride	>0.96		2425-54-9
1-Hexadecylchloride	>0.96		4860-03-1
Ethyl acetate	>0.995	< 0.0005	141-78-6

<sup>a</sup> Informed by the supplier.

another was not observed with the used ILs concentrations (below the CMCs).

For IFT measurements, experiments were conducted at different temperatures. The media was thermostated at desired temperatures using a calibrated thermostat (OPTIMA 740, Japan) with an uncertainty of  $\pm$  0.1 K. The organic and the aqueous phase samples were withdrawn to measure their density at different temperatures. Density was measured by means of an oscillating U-tube densimeter (Anton Paar DMA4500, Austria) with an uncertainty of  $\pm$  0.01 kg/m<sup>3</sup>, provided with automatic viscosity correction.

The performance and reliability of the method was examined based on the IFT value of pure n-butyl acetate + water system (binary saturated, without IL) at 298.2 K, and the result was compared with reported values in the literature. The obtained value of 14.0 mN/m is in agreement with reported values of 14.1 and 14.4 mN/m [25,26]. The maximum uncertainty for all measured IFT data was estimated as  $\pm$  0.1 mN/m.

Furthermore, to verifying the achievement of equilibrium condition, the IFT variation with drop formation time was investigated at different flow rates. The results with typical ILs solution of  $2.50 \cdot 10^{-3}$  mol/dm<sup>3</sup> at 298.2 K are presented in Fig. 1. When drops are formed rapidly, the ILs have no enough time to adsorb at the interface, and the dynamic IFT is dominant during short times of drop formation. As the time increases, each IL has further chance to continue accumulating at the interface. Eventually, when the time of drop formation becomes adequate (more than 30 s for drops in this work), the interface expansion occurs sufficiently slowly and no significant change appears with more drop formation times [27–29].

#### 3. Results and discussion

#### 3.1. Evaluation of experimental results

For each synthesized IL, aqueous phase concentrations ranging from very low to near CMC were utilized for each IL. In order to obtain temperature dependency, each solution was examined at six different temperatures, within 293.2–318.2 K. Density of each system was changed with increasing both concentration and temperature. The corresponding aqueous and organic phase densities varied within 991.04–998.80 kg/m<sup>3</sup> and 856.44–882.53 kg/m<sup>3</sup>. The phase densities and the IFT data at different temperatures as well as IL concentrations are listed in the supplementary information.

The measured IFT values were within the range of 13.4–14.0 mN/m for the pure system (without any IL), within 6.2–7.4 mN/m with  $[C_{12}mim][CI]$ , 4.5–5.7 mN/m with  $[C_{14}mim][CI]$  and 3.4–4.6 mN/m with  $[C_{16}mim][CI]$  under different temperatures. The IFT reduction percentage reaches to 55, 67 and 75%, by individual ILs, respectively.



**Fig. 1.** IFT variation as a function of drop formation time for ILs: ( $\blacksquare$ ), [ $C_{12}$ mim][Cl]; ( $\blacktriangle$ ), [ $C_{14}$ mim][Cl]; and ( $\bigcirc$ ), [ $C_{16}$ mim][Cl] at concentration of 2.50  $\cdot$  10<sup>-3</sup> mol/dm<sup>3</sup> and 298.2 K.

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In Fig. 2, the IFT variations versus ILs concentration are illustrated. The results show that presence of ILs leads to IFT reduction significantly at constant temperatures. Because of amphiphilic nature of the ILs, they migrate toward the interface and by increasing concentration, more adsorption occurs which causes more reduction in the IFT [30]. As can be seen, IFT decreases sharply (average reduction of 50, 61 and 69%) with very low ILs dosages to about  $1.00 \cdot 10^{-3}$  mol/dm<sup>3</sup> and then a mild variation is relevant by approaching to CMC. The interfacial activity of the used ILs appeared in the order of  $[C_{16}mim][Cl] > [C_{12}mim][Cl]$ ; revealing that more methylene bridge ( $-CH_2$ -) causes to impressive declining in the IFT values. It is since alkyl chain length is one important factor in the hydrophobicity nature of ILs [31].

In our recent work [13], effect of short alkyl chain ILs ([C<sub>n</sub>mim][Cl], n = 6, 7 and 8) on the IFT of n-butyl acetate + water system was studied. The results revealed that used ILs behave similar to surfactants and reduce the IFT significantly. In order to have comparison between the interfacial activity of short alkyl chain and long alkyl chain (with twice carbon atoms in alkyl chain) ILs, the IFT variations with effect of variety of ILs { $[C_6 \text{ to } C_{16} \text{mim}][Cl]$ } are presented in Fig. 3. The results obviously show significant declining in the IFT values with IL carbon numbers and that efficiency by long alkyl chains exceeds much of those by short alkyl chains. In this regard, the maximum percentage of the IFT reduction are 20, 26, and 33%, for ILs with n = 6, 7, and 8, respectively; however, rises to 55, 67, and 75%, using ILs with n = 12, 14, and 16. It has to mention that the highest concentration used for long alkyl chain ILs, was only 0.01 mol/dm<sup>3</sup> (10% of short alkyl chain ILs). Variations presented in Fig. 3 also show a remarkably linear decrease with carbon number till n = 14, and then a lower trend is relevant. The used ILs are different just due to their alkyl chain length and contain the same cationic segment and the counter anion. In this regard, the ILs with longer alkyl chain exhibit more hydrophobicity and consequently more interfacial activity [32]. As Fig. 4 represents, the required IL amount for declining IFT to a certain value, strongly decreases with alkyl chain length.

Finally, IFT decreases linearly with temperature in all cases (Fig. 5). The reduction is about 14% for each concentration within the used temperature range. Since the agitation kinetic of the molecules improves with increasing temperature, the IFT decreases gradually, as similarly reported for the effect of imidazolium ionic liquids on the surface tension [20].

#### 3.2. Theoretical model



In most studies, to relate the equilibrium IFT values to the substrate bulk concentration; Langmuir [33], Szyszkowski [34], and Frumkin [35]

**Fig. 2.** IFT variation as a function of concentration of  $[C_{12}mim][Cl]$  at: ( $\square$ ) 293.2 K, ( $\triangle$ ) 303.2 K, ( $\bigcirc$ ) 318.2 K,  $[C_{14}mim][Cl]$  at: ( $\blacksquare$ ) 293.2 K, ( $\blacktriangle$ ) 303.2 K, ( $\oslash$ ) 318.2 K and  $[C_{16}mim][Cl]$  at: ( $\blacksquare$ ) 293.2 K, ( $\bigstar$ ) 303.2 K, ( $\odot$ ) 318.2 K. Solid lines correspond to theoretical curves obtained by the Szyszkowski equation.



**Fig. 3.** IFT variation as a function carbon number in alkyl chain of IL with concentration of:  $1.00 \cdot 10^{-4} \text{ mol/dm}^3$  (**a**),  $1.00 \cdot 10^{-3} \text{ mol/dm}^3$  (**b**),  $5.00 \cdot 10^{-3} \text{ mol/dm}^3$  (**b**) and  $1.00 \cdot 10^{-2} \text{ mol/dm}^3$  (**b**); all at 298.2 K.

adsorption equations have been used. Among them, most experimental adsorption data for ILs have been well fitted by the Szyszkowski equation, which is obtained from the Gibbs and Langmuir adsorption equations [36]:

$$\gamma = \gamma_0 - 2RT\Gamma_m \ln(1 + K_L C_{IL}) \tag{2}$$

where  $\gamma_0$  is the IFT for pure chemical system ( $C_{IL} = 0$ ), and R and T are gas law constant and absolute temperature, respectively. Also,  $\Gamma_m$ ,  $K_L$ , and  $C_{IL}$  are the maximum interfacial concentration (saturated interface), the Langmuir equilibrium adsorption constant and the IL bulk concentration, respectively. In a simple convention, the factor 2 stands for the dissociation of each ionic surface active substance into its cation and anion. Correspondingly, Szyszkowski equation was used here to fit the experimental data, obtained with each IL bulk concentrations at constant temperatures. The coefficient of determination,  $R^2$  was calculated using [37]:

$$R^{2} = 1 - \frac{\sum_{i=1}^{N} \left(\gamma_{cal,i} - \gamma_{exp,i}\right)^{2}}{\sum_{i=1}^{N} \left(\overline{\gamma} - \gamma_{exp,i}\right)^{2}}$$
(3)

where *N*,  $\gamma_{\rm cal}$ ,  $\gamma_{\rm exp}$ , and  $\overline{\gamma}$  stand for the number of data, the calculated IFT by the model, the experimental IFT and the average of all the



**Fig. 4.** IFT variation as a function of ILs concentration:  $(\Box)$ ,  $[C_6mim][Cl]; (\Delta)$ ,  $[C_7mim][Cl]; (\bigcirc)$   $[C_8mim][Cl]; (\blacksquare)$ ,  $[C_{12}mim][Cl]; (\blacktriangle)$ ,  $[C_{14}mim][Cl]; (\bullet)$   $[C_{16}mim][Cl]$  at: 298.2 K.



**Fig. 5.** IFT variation as a function of temperature in the presence of ILs: (**T**),  $[C_{12}mim][CI]; (\blacktriangle), [C_{14}mim][CI]; and (•), [C_{16}mim][CI] at typical concentration of 2.50 · 10<sup>-3</sup> mol/dm<sup>3</sup>.$ 

appropriate experimental values, respectively. The obtained  $R^2$  values, listed in Table 2 (ranged within 0.9777–0.9894), indicate consistent fittings with the Szyszkowski model. As well, solid lines in Fig. 2 are theoretical curves that show close agreement with the experimental data.

One significant result from this study is the ideal IL behavior at the interface of n-butyl acetate + water, implied from Szyszkowski equation. However, in our previous study [27] with toluene + water system, non-ideal interaction between adsorbed ILs was relevant, principally attributed to electrostatic repulsions. The difference can be ascribed to the interaction between IL molecules with both organic and aqueous phases. By considering the utilized IL structure (presented in supplementary data), it is clear that there is an acidic hydrogen on carbon number 2 between two electronegative nitrogen atoms. As a result, there is a high chance to form hydrogen bonds between this hydrogen and electronegative atoms in both n-butyl acetate and water molecules. This interaction decreases or totally removes the repulsion between absorbed ILs at the interface causing an ideal monolayer adsorption. Therefore, the Szyszkowski equation can be adequately used to fit the

#### Table 2

Maximum interface excess,  $\Gamma_{\rm m}$ , Langmuir equilibrium adsorption constant,  $K_{\rm L}$ , minimum area occupied by a molecule,  $A_{\rm m}$ , standard free energy of adsorption,  $\Delta G_{\rm ads}$ , and coefficient of determination,  $R^2$ , for adsorption of ILs at different temperatures<sup>a</sup>.

<i>T</i> (K)	$10^6 \cdot \Gamma_m$ (mol/m <sup>2</sup> )	$\frac{10^{-3} \cdot K_{\rm L}}{({\rm m}^3/{\rm mol})}$	$\frac{10^{18} \cdot A_{\rm m}}{(\rm nm^2)}$	$-\Delta G_{ads}$ (kJ/mol)	<i>R</i> <sup>2</sup>			
[C <sub>12</sub> mim][C]]								
293.2	88.31	2.49726	1.06	264.45	0.9796			
298.2	86.72	2.57991	1.10	267.64	0.9791			
303.2	84.20	2.63845	1.16	271.12	0.9784			
308.2	81.16	2.68925	1.21	276.91	0.9789			
313.2	76.91	2.71687	1.27	282.24	0.9777			
318.2	70.09	2.72111	1.31	287.66	0.9781			
[C <sub>14</sub> mim][Cl]								
293.2	96.37	3.02677	0.91	306.25	0.9888			
298.2	94.12	3.12832	0.98	311.82	0.9885			
303.2	90.90	3.19517	1.04	317.86	0.9889			
308.2	87.36	3.23724	1.09	324.19	0.9884			
313.2	83.01	3.26677	1.13	336.44	0.9886			
318.2	78.42	3.27351	1.17	343.61	0.9878			
[C <sub>16</sub> mim][Cl]								
293.2	103.61	3.52616	0.81	355.14	0.9876			
298.2	101.29	3.62922	0.86	361.86	0.9871			
303.2	98.25	3.70326	0.90	369.75	0.9883			
308.2	94.31	3.75849	0.98	377.48	0.9894			
313.2	90.06	3.78579	1.06	385.19	0.9880			
318.2	84.61	3.79901	1.13	396.73	0.9888			

<sup>a</sup> The standard uncertainty: u(T) = 0.1 K.

experimental data. In this regard, the adsorption parameters including maximum interface excess,  $\Gamma_m$ , and the Langmuir equilibrium adsorption constant,  $K_L$ , were obtained (Table 2).

The maximum interface excess,  $\Gamma_{\rm m}$ , is the concentration at the saturated interface. This value explains effectiveness of adsorption in which maximum adsorption is achieved. Its variation with temperature is depicted in Fig. 6 for each of the used ILs. It is clear that with increasing temperature, a decreasing variation in  $\Gamma_{\rm m}$  is observed as a result of disrupting water molecules around the hydrophobic portion which causes less transfer of ILs toward the interface [38].

The maximum interface excess increases with methylene bridge  $(-CH_{2}-)$  in the IL tail since longer alkyl chains give higher hydrophobicity and leads to more molecules adsorption at the interface [39]. As a result, obtained  $\Gamma_m$  values for  $[C_{16}mim][Cl]$  is more than those of  $[C_{14}mim][Cl]$  and  $[C_{12}mim][Cl]$ .

Corresponding to  $\Gamma_m$ , the minimum area occupied by an adsorbed molecule at the interface,  $A_m$ , can be obtained from the following equation [40]:

$$A_{\rm m} = \frac{1}{\Gamma_{\rm m} N_{\rm Av}} \tag{4}$$

in which,  $N_{Av}$  is the Avogadro's number.

The calculated  $A_m$  values, for each IL at different temperatures, are listed in Table 2. The results indicate that when concentration decreases at the interface, each molecule occupies more area at higher temperatures. On the other hand, compact monolayers with lesser occupied areas are formed by the IL molecules with longer alkyl chain length.

The adsorption tendency, on the other hand, is described by Langmuir equilibrium adsorption constant,  $K_L$ . Its variation with temperature is presented in Fig. 7. The results demonstrate that adsorption tendency increases with both temperature and alkyl chain length. At higher temperatures, intensifying of motions occurs; therefore, more tendencies of the IL molecules toward the interface are expected. As well, it is evident that [C<sub>16</sub>mim][Cl] has the highest adsorption tendency than others because of more hydrophobicity nature and more migration tendency toward the interface.

Related to equilibrium constant, another important parameter is standard free energy of adsorption,  $\Delta G_{ads}$ , which can be obtained from [38]:

$$\Delta G_{ads} = -2RT \ln\left(\frac{K_{L}\rho'}{2}\right) \tag{5}$$

where  $\rho'(=\rho_w/18)$  is the molar concentration of water for a given temperature.



**Fig. 6.** Maximum interface excess as a function of temperature: ( $\blacksquare$ ),  $[C_{16}mim][Cl]$ ; ( $\blacktriangle$ ),  $[C_{14}mim][Cl]$ ; and ( $\bullet$ ),  $[C_{12}mim][Cl]$ .



**Fig. 7.** Equilibrium adsorption constant as a function of temperature: (**T**),  $[C_{16}mim][Cl];$  (**A**),  $[C_{14}mim][Cl];$  and (**O**),  $[C_{12}mim][Cl].$ 

As the final point, the standard free energy of IL adsorption, at different temperatures, has negative values (Table 2); implying that the adsorption is spontaneous in all cases.

#### 4. Conclusions

Established upon the IFT measurements, the adsorption of amphiphilic synthesized long chain imidazolium ILs,  $[C_{12}mim][Cl]$ ,  $[C_{14}mim][Cl]$ , and  $[C_{16}mim][Cl]$  at the n-butyl acetate + water interface was investigated. The used ILs significantly decrease the interfacial tension of the system due to their surfactant nature. Longer alkyl chain ILs adsorb at the interface are more effectively related to their higher hydrophobicity. Accordingly, the maximum IFT reductions were 55, 67, and 75%, respectively, within applied temperature ranges. Besides, the IFT values were decreased linearly with temperature.

The Szyszkowski adsorption equation was satisfactorily applied to reproduce the experimental data. Accordingly, IL molecules behave ideal with no interaction at the interface and the maximum interface excess and the adsorption tendency show dependency on alkyl chain length, as well as temperature. Totally, maximum interface excess decreases with temperature; however, increases when hydrophobicity of ILs increase due to longer alkyl chain. It is while the Langmuir equilibrium adsorption constant increases with either increase of temperature or use of longer alkyl chain length.

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#### Appendix A. Supplementary data

The supplementary information of the ILs analyzing spectra and their specification and the IFT measurement details are given in the attached file. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.molliq.2015.08.056.

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