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Interfacial Tension of *n*-Alkane and Ionic Liquid Systems

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Liquid−liquid interfacial tension of four 1-alkyl-3-methylimidazolium ([Cn-mim], $n = 5, 6, 7, 8$) based ionic liquids (ILs) and two *n*-alkanes ($n = 6, 7$) are reported in the temperature range from (283.15 to 343.15) K at atmospheric pressure using the platinum ring method. The interfacial tensions show a linear decrease with increasing temperature. The obtained data were correlated by an empirical equation, and fitting interfacial tension parameters are presented.

Introduction

Ionic liquids (IL) are a class of compounds that are being extensively studied because of their unusual properties. In particular, these liquids have very low vapor pressures, and thus, they have great potential as green solvents for industrial processes such as chemical synthesis, liquid−liquid extraction, gas−liquid absorption, and liquid membrane separations.[1] A rapidly developing application area for ILs is that of two-phase homogeneous catalytic reaction, where one phase containing the catalyst is immiscible with the second phase containing the reactant and products. Such a catalysis is believed to occur at the interface between the IL and the organic phase and should be dependent on the access of the catalyst to the surface and the transfer of material across the interface.[2] A clear understanding of the mechanisms behind the catalysis process requires a more detailed examination of the surface properties of ILs.[3]

Interfacial tension is an important property of liquid−liquid interfaces. This property affects the hydrodynamics and contact of phases which relate to mass transfer purposes. The data of interfacial tension are required by chemical engineers for the design of liquid−liquid contactors. Interfacial tension has an effect on the droplet coalescence and two-phase separation. The larger interfacial tension is helpful for droplet coalescence and the liquid−liquid two-phase separation. On the other hand, the larger interfacial tension makes it difficult to disperse the two-phase mixture, in this case, more energy is required to further disperse the two phases. So the design of industrial extraction contactors requires knowledge of interfacial tension data.

To calculate these parameters, one of the physical properties that must be known is interfacial tension.[4] The air−liquid interfacial tension (surface tension) data for a pure IL system are relatively rich in the literature,[5] while those for the mixture system of ILs and molecular solvents are still limited. A few recently published works have investigated the surface tension of binary mixtures containing an IL with miscible molecular solvents such as alcohols.[6−8] However, the studies on liquid−liquid interfacial tension of ILs and immiscible molecular solvents are very scarce.

The current work presents the liquid−liquid interfacial tension measurements at atmospheric pressure of closely related ILs: 1-pentyl-3-methylimidazolium hexafluorophosphate, $[C_5mim]PF_6$, 1-hexyl-3-methylimidazolium hexafluorophosphate, $[C_6mim]PF_6$, and 1-octyl-3-methylimidazolium hexafluorophosphate, $[C_8mim]PF_6$, with hexane in the temperature range from (283.15 to 343.15) K; and 1-butyl-3-methylimidazolium hexafluorophosphate, $[C_4mim]PF_6$, 1-pentyl-3-methylimidazolium hexafluorophosphate, $[C_5mim]PF_6$, and 1-hexyl-3-methylimidazolium hexafluorophosphate, $[C_6mim]PF_6$, with heptane in the temperature range from (283.15 to 343.15) K. The obtained interfacial tension was correlated by an empirical equation The influence of the cation alkyl chain length on the interfacial tension was discussed.

Experimental Methods

Four imidazolium-based ILs, $[C_4mim]PF_6$ (mass fraction > 99 %), $[C_5mim]PF_6$ (mass fraction > 99 %), $[C_6mim]PF_6$ (mass fraction > 99 %), and $[C_8mim]PF_6$ (mass fraction > 99 %), were obtained from Shanghai Chengjie Chemical Co. To reduce the water content, all of the IL samples were dehydrated under vacuum at 80 °C for at least 48 h prior to the measurements. Water content in the ILs, determined by Karl Fisher titration, was below 0.03 %. Heptane (mass fraction > 99 %) and hexane (mass fraction > 99 %) were supplied by Beijing Chemical Reagent Co. and were used without further purification.

The interfacial tension of the samples was measured with a DCAT21 tensiometer from Dataphysics Ltd. using a Du-Noüy ring taking into account the Zuidema Waters correction. The method has been used by a number of investigators.[9−13] To avoid surface contamination and the adsorption of water, all surface tension measurements were performed in nitrogen atmosphere. The measurements were carried in the temperature range from (283.15 to 343.15) K. Samples were measured in a closed measuring cell with a volume of about 50 cm^3, and the temperature was controlled within ± 0.5 K by circulating temperature-regulated water around the measuring cell. Before beginning a series of experiments, the platinum/iridium alloy ring (radius, 9.4425 mm; wire radius, 0.185 mm) and vessel were thoroughly cleaned by immersion in a concentrated solution of nitric acid for several hours. Then both were rinsed with distilled water, flame-dried, washed again with distilled water, and dried. The unit operates using the ring method where a ring immersed below either the air−liquid or the liquid−liquid interface (for interfacial tension) is raised slowly while measuring the force. The force required to raise the ring just at a

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Table 1. Interfacial Tension for IL/Alkane Systems at Different Temperatures

IL/alkane	*T*/K 283.15	293.15	303.15	313.15	323.15	333.15
	γ/mN·m^{-1}					
[C$_5$mim]PF$_6$/hexane	12.37	12.11	12.00	11.93	11.78	11.67
[C$_6$mim]PF$_6$/hexane	9.01	8.90	8.83	8.84	8.73	8.68
[C$_8$mim]PF$_6$/hexane	4.89	4.77	4.66	4.52	4.45	4.46
[C$_4$mim]PF$_6$/heptane	14.81	14.69	14.67	14.59	14.50	14.41
[C$_5$mim]PF$_6$/heptane	12.23	12.12	12.02	11.90	11.63	11.53
[C$_6$mim]PF$_6$/heptane	8.86	8.74	8.73	8.69	8.54	8.47

particular lamella height, which is the distance of the ring, forms the liquid interface. This maximum force is directly related to the surface or interfacial tension with knowledge of the density. The density determination of the two liquid phases was performed using a densimeter (MYX-1). The repeatability of the density measurement was ± 0.0002 g·cm^{-3}. The density measuring cell was thermostatted with a temperature stability of ± 0.02 K.

Each value reported was an average of 10 measurements, where the maximum deviation from the average value was always less than 0.5 %. The uncertainty of the measurements was ± 0.1 mN·m^{-1}. After the first few measurements, there is a tendency to obtain a practically constant value. The performance of the tension balance was checked by measuring the surface tension of double-distilled water. The surface tension of double-distilled water at 298.15 K was measured as 71.97 mN·m^{-1} which is consistent with a literature report[14] of 71.99 mN·m^{-1}. The measured liquid interfacial tension value of the immiscible water−hexane system at 293.15 K was 49.9 mN·m^{-1}, which is in accordance with the value of 49.4 mN·m^{-1} obtained at the 293.15 K using the same technique.[11]

For the liquid interfacial tension measurements, the mixture of hexane−heptane and IL was vigorously stirred by using a magnetic rotor at the required constant temperature for at least 12 h to reach the equilibrium. Afterward, the mixture was permitted to stand for several hours to completely separate into two transparent phases at the experimental temperature. Samples of the organic and the IL phases were withdrawn to measure the density and the liquid interfacial tension. The surface tension of each liquid phase was also measured separately.

Results and Discussion

The interfacial tension of IL/alkane systems were measured at different temperatures and are listed in Table 1. For all of the IL/alkane systems studied in this research, the interfacial tension data decreases with temperature to a very small extent in the temperature range from (283.15 to 343.15) K. The measured interfacial tension decreases with increasing alkyl chain length of the IL at the same temperature for both the IL/heptane system and the IL/hexane system as shown in Figures 1 and 2. For example, when the carbon number in alkyl chain of the IL increases from 4 to 6 for IL/heptane at 293.15 K, the interfacial tension falls from (14.69 to 8.74) mN·m^{-1}.

Matsuda et al.[15] investigated the [C$_6$mim]PF$_6$/hexane system by the pendant drop method in temperatures from (288.15 to 308.15) K, and their results show that there are no change for the interfacial tension value with the increase of temperature. This phenomenon is different from that reported for the [C$_6$mim]PF$_6$/hexane system in the current study. In the temperature range from (283.15 to 343.15) K, the interfacial tension values of [C$_6$mim]PF$_6$/hexane decrease with temperature to a small extent and are in the range of (9.01 to 8.68) mN·m^{-1} for this study, which compares with the value of 8.36 mN·m^{-1} at (288.15 to 308.15) K reported by Matsuda et al. Ahosseini and co-workers[10] have measured the interfacial tension of [HMIm]-[Tf$_2$N]/1-octane system using the Du Noüy ring method. Their results show that the interfacial tension decreases with temperature to a small extent at (283.15 to 298.15) K. This phenomenon is similar to our results. The interfacial tension of [C$_n$mim][NTf$_2$]/*n*-alkane systems determined by Gardas and co-workers[16] using the pendant drop method is found to slightly decrease with an increase in temperature from (293 to 313) K. This trend is also similar to our results.

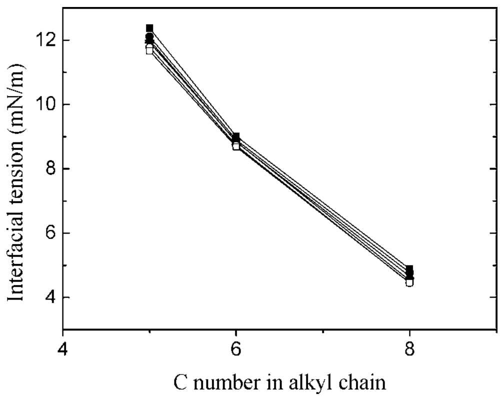

Figure 1. Interfacial tension of hexane/ILs at different temperatures. ■, 283.15 K; ●, 293.15 K; ▲, 303.15 K; ▼, 313.15 K; ○, 323.15 K; □, 333.15 K.

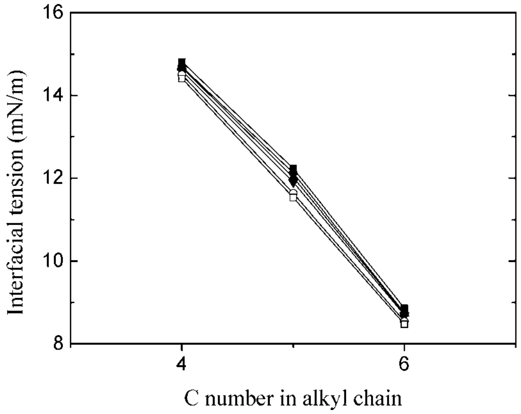

Figure 2. Interfacial tension of heptane/ILs at different temperatures. ■, 283.15 K; ●, 293.15 K; ▲, 303.15 K; ▼, 313.15 K; ○, 323.15 K; □, 333.15 K.

Interfacial tension values of alkane/ILs are considerably small compared with the surface tension of pure IL and alkane in this study. For example, as shown in Figures 3 and 4 and Table 2, the surface tension data of pure [C$_5$mim]PF$_6$ and [C$_4$mim]PF$_6$ are in the range of (42.7 to 40.4) mN·m^{-1} and (48.6 to 45.5) mN·m^{-1}, respectively, whereas the interfacial tension values are only in the range of (12.37 to 11.67) mN·m^{-1} and (14.81 to 14.41) mN·m^{-1} for [C$_5$mim]PF$_6$/hexane and [C$_4$mim]PF$_6$/heptane, respectively.

The increase in temperature from (283.15 to 343.15) K results in a linear decrease of the interfacial tension as are represented typically by Figures 5 and 6. The experimental interfacial tension data of the system can be expressed through the empirical eq 1, which has been extensively used by a number of authors to investigate the temperature dependence of the interfacial tension and surface tension.[13,17−21]

$$\gamma/\text{mN}\cdot\text{m}^{-1} = K_1 - K_2(T/\text{K}) \tag{1}$$

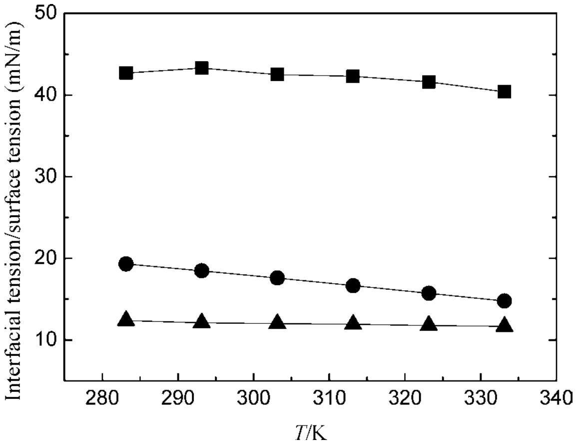

Figure 3. Interfacial tension of the [C_5mim]PF_6/hexane system with temperature compared to the pure component surface tensions: ■, [C_5mim]PF_6; ●, hexane; ▲, [C_5mim]PF_6/hexane.

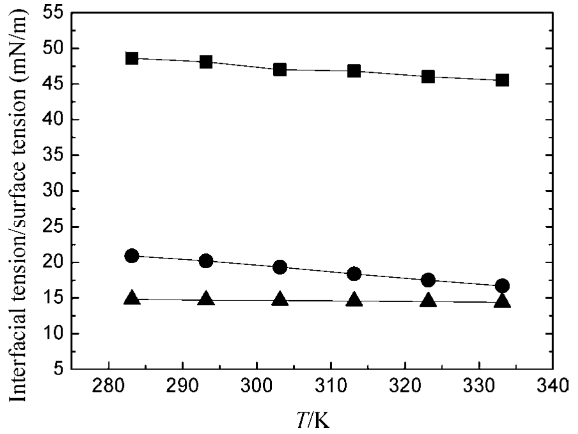

Figure 4. Interfacial tension of the [C_4mim]PF_6/heptane system with temperature compared to the pure component surface tensions: ■, [C_4mim]PF_6; ●, heptane; ▲, [C_4mim]PF_6/heptane.

Table 2. Surface Tension for Pure ILs and Alkanes at Different Temperatures

	T/K					
pure substances	283.15	293.15	303.15	313.15	323.15	333.15
	γ/mN·m^{-1}					
[C_4mim]PF_6	48.60	48.11	47.00	46.79	46.01	45.50
[C_5mim]PF_6	42.70	43.29	42.49	42.30	41.58	40.40
[C_6mim]PF_6	39.10	38.89	38.70	38.20	37.51	36.60
[C_8mim]PF_6	35.78	35.16	34.60	33.89	33.14	32.67
hexane	19.31	18.49	17.58	16.66	15.72	14.78
heptane	20.90	20.20	19.32	18.38	17.51	16.69

where K_1 and K_2 are the interfacial tension parameters, obtained by fitting, whose values are listed in Table 3. The absolute average deviation (AAD), defined as

$$\mathrm{AAD} = \left[\frac{1}{c}\sum_{i=1}^{c}\frac{|\gamma_{i,\mathrm{exp}} - \gamma_{i,\mathrm{cal}}|}{\gamma_{i,\mathrm{exp}}}\right]\cdot 100 \qquad (2)$$

was calculated. In this equation, c is the number of data points. The absolute average deviations of the calculated surface tension from the experimental values are presented in Table 3. The AADs obtained in the correlation are in the range of (0.10 to 0.77) %, which appear to satisfactory.

A remarkably simple expression for interfacial tension was proposed by van Oss.[22] van Oss expressed the interfacial tension, γ, as a function of the corresponding air−liquid surface tension of γ_{IL} and γ_{alk}, using

$$\gamma^{\mathrm{IL\text{-}alk}} = \gamma^{\mathrm{IL}} + \gamma^{\mathrm{alk}} - 2\phi\sqrt{\gamma^{\mathrm{IL}}\gamma^{\mathrm{alk}}} \qquad (3)$$

where ϕ is the interaction parameter that is closely correlated to the contribution from polar interaction to the interfacial tension;[10] ϕ is near zero for nonpolar−nonpolar interfaces, less than one for nonpolar−polar systems, and greater than one for the polar−polar system. The ϕ value at different temperatures is shown in Table 4. The parameter ϕ increases slightly as the alkyl chain of IL in the 1-position of the cation is lengthened for the series of [$C_n$mim]PF_6/hexane systems; a similar effect occurs for the [$C_n$mim]PF_6/heptane systems. For example, when the alkyl chain of IL in the 1-position of the cation increases from 4 to 6, the ϕ value increases from 0.8599 to 0.8983 at 293.15 K for [$C_n$mim]PF_6/heptane systems. All of the parameters of IL/alkane systems in this study are smaller than one, and this results in agreement with a nonpolar−polar system.

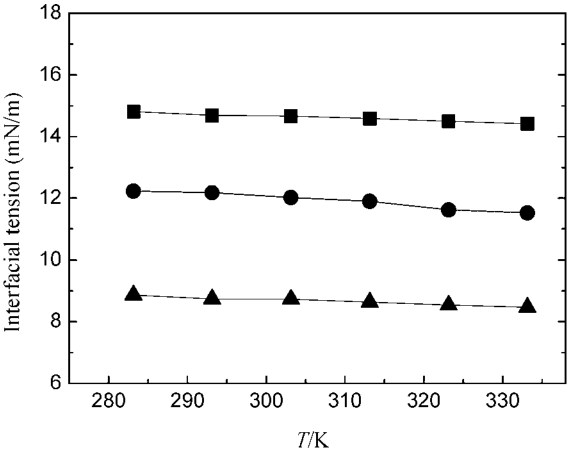

Figure 5. Interfacial tension of ILs/heptane: ■, [C_4mim]PF_6/heptane; ●, [C_5mim]PF_6/heptane; ▲, [C_6mim]PF_6/heptane.

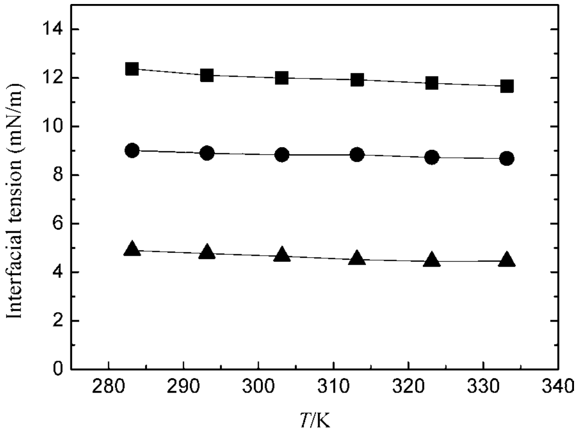

Figure 6. Interfacial tension of ILs/hexane: ■, [C_5mim]PF_6/hexane; ●, [C_6mim]PF_6/hexane; ▲, [C_8mim]PF_6/hexane.

Table 3. Interfacial Tension Parameters K_1 and K_2 for the System

	K_1	$K_2\cdot10^{-2}$	AAD (%)
[C_5mim]PF_6/hexane	15.99	1.303	0.29
[C_6mim]PF_6/hexane	10.75	0.622	0.25
[C_8mim]PF_6/hexane	7.508	0.935	0.77
[C_4mim]PF_6/heptane	16.96	0.760	0.10
[C_5mim]PF_6/heptane	16.59	1.518	0.33
[C_6mim]PF_6/heptane	11.00	0.757	0.29

Table 4. Model Interaction Parameters for ILs/Alkanes at Different Temperatures

IL/alkane	T/K 283.15	293.15	303.15	313.15	323.15	333.15
	ϕ					
[C_5mim]PF_6/hexane	0.8643	0.8779	0.8795	0.8859	0.8903	0.8903
[C_6mim]PF_6/hexane	0.8989	0.9040	0.9095	0.9121	0.9161	0.9180
[C_8mim]PF_6/hexane	0.9548	0.9586	0.9633	0.9686	0.9728	0.9782
[C_4mim]PF_6/heptane	0.8579	0.8599	0.8571	0.8625	0.8634	0.8669
[C_5mim]PF_6/heptane	0.8598	0.8677	0.8690	0.8748	0.8797	0.8774
[C_6mim]PF_6/heptane	0.8944	0.8983	0.9013	0.9047	0.9067	0.9067

Conclusions

Liquid−liquid interfacial tension of imidazolium-based ILs and two *n*-alkanes ($n = 6, 7$) were measured in the temperature range from (283.15 to 343.15) K at atmospheric pressure using the Du Noüy ring platinum ring method. The interfacial tension data decrease with temperature to a very small extent in the temperature range from (283.15 to 343.15) K for all of the IL/alkane systems studied in this research. The measured interfacial tension decreases with increasing alkyl chain length at the same temperature for IL/alkane systems. For example, when the C number in the alkyl chain increases from 4 to 6 for IL/heptane at 293.15 K, the interfacial tension falls from (14.69 to 8.74) $\mathrm{mN \cdot m^{-1}}$. The interfacial tensions of the IL/alkane system show a linear decrease with increasing temperature. The obtained data were correlated by an empirical equation, and the absolute average deviations of the calculated surface tension from the experimental values are in the range of (0.10 to 0.77) %.

The interfacial tension was expressed as a function of the air−liquid surface tension of ILs and alkanes; the corresponding interaction parameter is just less than one with a slight temperature dependence in accordance with a nonpolar−polar mixture.

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