

Study on the Surface Property of Surfactant Ionic Liquids Solutions

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Abstract: The surfactant TX-100 can be dissolved in ionic liquid bmimPF₆ and decrease the surface tension of 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆) solutions. Here, we confirmed that in this new system, the pure solvents need rearrangement at the air-water interface at the initial stage. The dynamic surface tension (DST) study shows that at the initial adsorption stage, the adsorption model of surfactant accords with the diffusion-controlled adsorption mechanism, and the dilute ionic liquids solutions is further close to the diffusion-controlled adsorption.

Keywords: Dynamic surface tension, ionic liquids, adsorption.

Ionic liquids (ILs) are receiving much attention as a class of neoteric solvents and have been used widely as solvents for organic synthesis¹⁻⁵, chemical separations⁶⁻⁹. As an ideal substitute for organic solvents, they afford significant environmental benefits and can contribute to green chemistry.

Surfactant tension measurement can afford much valuable information, it is necessary to measure the surfactant tension for the surfactants ILs solutions. Furthermore, DST is also an important property as it governs many important industrial processes¹⁰. To our knowledge, the study on dynamic surface tension of ILs solutions has not been reported so far. The study is significant to further understand the adsorption mechanisms of surfactants from theoretical viewpoint.

Experimental

The surfactant TX-100 was purchased from Merck. Water was doubly distilled and used throughout the experiments. Ionic liquid bmimPF₆ used in our experiments was prepared according to the literature¹¹. Equilibrium surface tensions were measured using a Krüss K12 tension apparatus. DSTs were measured by MBP tensiometer. The samples were thermostated to ± 0.1 °C.

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Results and Discussion

Figure 1 shows the surface tension of TX100 of ionic liquid solution as a function of surfactant concentration at 25°C. We found that the dissolution of TX-100 in bmimPF₆ can depress the surface tension. This phenomenon shows that there are ionic liquids solvatophobic interactions with the hydrocarbon portion of the surfactants. The main differences (see **Figure 2**) between ILs and aqueous solutions are that the initial surface tension of the neat ILs is lower and the cmc (about 0.01 mol/L) is greatly higher than that (about 1.7×10⁻⁴ mol/L) of the same surfactant aqueous solution. TX-100 contains polyoxyethylene groups and each individual subunit of these groups contains oxygens with lone pair electrons that are capable of accepting hydrogen or interact with positive charge groups, therefore there are enhanced interaction between TX-100 and bmimPF₆. So, the polyoxyethylene group is “ILs-philic”. Therefore, the ILs systems which possess the surface activity and formed micelle will be further determined their properties of DST.

The asymptotic Ward and Tordai equation describes the diffusion-controlled adsorption $\Gamma(t)$ of surface active molecules at a fresh interface¹². These asymptotic equations are given by Miller *et al.*¹³.

$$\text{short times} \quad \gamma(t)_{t \rightarrow 0} = \gamma_0 - 2RTc \left(\frac{Dt}{\pi} \right)^{1/2} \quad (1)$$

$$\text{and long times} \quad \gamma(t)_{t \rightarrow \infty} = \gamma_{eq} + \frac{RT\Gamma^2}{2c} \left(\frac{\pi}{Dt} \right)^{1/2} \quad (2)$$

The parameters c , Γ , and D represent the bulk concentration, equilibrium surface and monomer diffusion coefficient of the surfactant. If the adsorption is purely diffusion controlled, then Eq. 1 and 2 should account for the tension decay. DST measurements were made between 0.003 and 0.07 mol/L for TX-100 surfactant concentration. Example $\gamma(t)$ decays of the same concentrations ILs and aqueous solutions are shown in **Figure 3**. As can be seen from **Figure 3**, the surfactant TX100 is more active in water than ILs. $\gamma(t)_{t \rightarrow 0}$ is in some extent larger than γ_0 of neat bmimPF₆. For dilute aqueous solutions, the similar phenomenon is also observed and argued diffusely¹⁴. However, for thick surfactant aqueous solutions, the phenomenon can not be obtained. The reason is that surface adsorption is so fast that surface tension decrease can not be captured using current MBP tensiometer. The viewpoint, that the pure solvents need rearrangement at the air-water interface at the initial stage, is generally accepted¹⁴.

In this neoteric ILs solvent system, this phenomenon is much more obvious, which is correlative with the complicated structure and properties of ILs. High viscosity and low diffusion coefficient of ILs perhaps contribute to the slow rearrangement considering bmimPF₆ containing a butyl on the imidazolium ring, these short hydrophobic tails maybe protend out the air-liquid interface like surfactant tails. The premise is based on that bmimPF₆ can slightly decrease surface tension of water. Thus, the anions PF₆⁻ also rearrange accordingly due to the rearrangement of cations. When a new interface forms in bmimPF₆, the rearrangement time is much longer than neat water. As a novel system, our results further confirm the above viewpoint.

Figure 1 Surface tension of TX-100 ionic liquid solution as a function of surfactant concentration at 25°

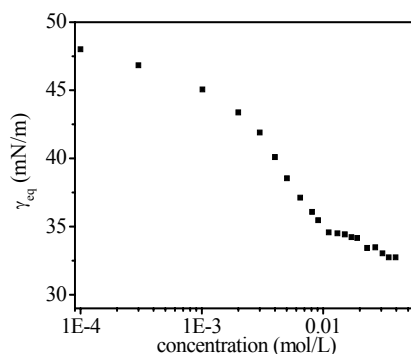


Figure 2 Surface tension of TX-100 aqueous solution as a function of surfactant molar concentration at 25°C

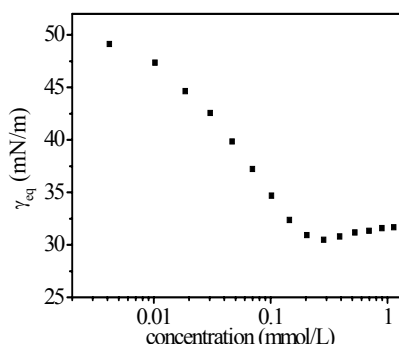


Figure 3 DST for TX-100 bmimPF₆ solution plotted vs. surfactant concentration (cloudy point appears for 0.01 mol/L aqueous solution at 25°C)

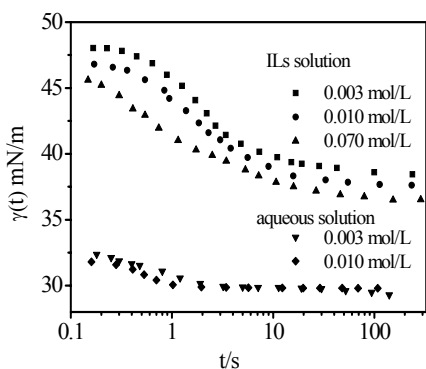


Figure 4 DST for TX-100 ionic liquids solutions plotted vs. $t^{1/2}$ and the lines are least squares fits to the data as $t \rightarrow 0$

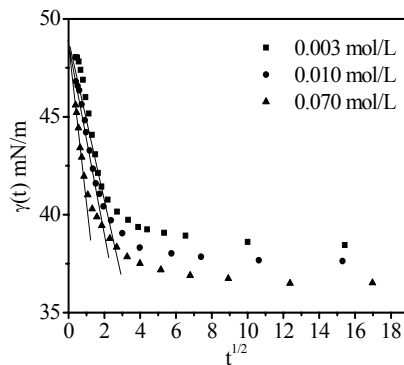


Figure 4 shows the $\gamma(t)$ decays for TX-100 plotted vs $t^{1/2}$, and in this representation the short time data linearize as predicted by Eq 1. The lines are least-squares fits over an appropriate time range, with the intercept fixed close to γ_0 of bmimPF₆, suggesting a near diffusion-controlled adsorption at the initial adsorption stage, which is accordance with the result reported previously¹⁵. Eq 1 can describe the adsorption stage well before about 4s, but poor agreement with long time. This behavior is entirely consistent with the presence of a weak adsorption barrier. Thus, the DST decays belong to the mixed diffusion-controlled adsorption mechanism as proposed by Liggieri¹⁶.

In addition, adsorption mechanism at low concentration is close to diffusion controlled. Recently, Eastoe *et al.*¹⁷ found that for a surfactant aqueous solution, there is some evidence for a weaker adsorption barrier. Later, Chen *et al.*¹⁸ have investigated the DST of octadecyl dimethylammionum chloride and found that the higher the concentration of surfactant system, the higher the adsorption barrier. Chai *et al.*¹⁹ have also discovered the similar results through investigating CTAB. This phenomenon can

be explained as follows: when the surfactant concentration is quite low, the equilibrium surface coverage is low and every molecule arriving at the surface is likely to arrive at an empty site, the monomer can be instantaneously adsorbed at the surface and the diffusion process from the bulk to subsurface is close to the rate-controlling step, and thus the adsorption barrier is very small. With the increase of surfactant concentration, the number of monomers adsorbed at the surface gradually increase, and thus, surface pressure π increases, which induces the appearance of energy barrier^{10,20}. In this case, the mixed diffusion controlled adsorption mechanism dominates at this stage. Similarly, when the surfactant concentration is high, the adsorption process is controlled by a diffusion step at the beginning, toward the end, it changes to a mixed diffusion adsorption mechanism^{10,17}.

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References

1. T. Welton, *Chem. Rev.*, **1999**, *35*, 2071.
2. T. D. Avery, N. F. Jenkins, M. C. Kimber, *et al.*, *Chem. Commun.*, **2002**, 28.
3. J. G. Huddleston, H. D. Willauer, R. P. Swatoski, *et al.*, *Chem. Commun.*, **1998**, 1765.
4. H. M. Zerth, N. M. Leonard and R. S. Mohan, *Org. Lett.*, **2003**, *5*, 55.
5. M. Smietana and C. Mioskowski, *Org. Lett.*, **2001**, *3*, 1037.
6. J. L. Anderson, J. Ding, T. Welton, D. W. Armstrong, *J. Am. Chem. Soc.*, **2002**, *124*, 14247.
7. S. Chun, S. V. Dzyuba, and R. A. Bartsch, *Anal. Chem.*, **2001**, *73*, 3737.
8. L. A. Blanchard and J. F. Brennecke, *Ind. Eng. Chem. Res.*, **2001**, *40*, 287.
9. B. P. Binks, A. K. F. Dyab and P. D. I. Fletcher, *Chem. Commun.*, **2003**, 2540.
10. J. Eastoe, J. S. Dalton, *Adv. Coll. Interf. Sci.*, **2000**, *85*, 103.
11. J. M. Zhang, C. H. Yang, Z. S. Hou, *et al.*, *New J. Chemistry*, **2003**, *27*, 333.
12. A. F. H. Ward, L. Tordai, *J. Chem. Phys.*, **1946**, *14*, 453.
13. V. B. Fainerman, A. V. Makievski, R. Miller, *Colloids and Surfaces A.*, **1994**, *87*, 61.
14. Y. Li, *Ph.D. thesis*, ShanDong University, China, **1999**.
15. J. Eastoe, J. S. Dalton, P. G. A. Rogueda, *et al.*, *J. Colloid and Interface Sci.*, **1997**, *188*, 423.
16. L. Liggieri, F. Ravera, A. Passerone, *Colloids and Surfaces A*, **1996**, *114*, 351.
17. J. Eastoe, J. S. Dalton, *Langmuir*, **1998**, *14*, 5719.
18. W. J. Chen, G. Z. Li, J. L. Chai, Y. Li, Z. G. Zhang, *Acta Chimica Sinica*, **2002**, *60*, 669.
19. J. L. Chai, G. Y. Zhang, G. Z. Li, Y. Li, X. G. Xu, *Acta Chimica Sinica*, **2001**, *59*, 2122.
20. J. Eastoe, J. Dalton, P. Rogueda, D. Sharpe, J. F. Dong, *Langmuir*, **1996**, *12*, 2711.

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