

Synthesis and Solution Properties of Novel Nonionic Functional Polyurethane Surfactants

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ABSTRACT: A series of novel nonionic functional polyurethane surfactants were synthesized by the polycondensation of 2,4-toluene diisocyanate with poly(propylene oxide) (weight-average molecular weight = 400, 1000, or 2000) and monoallyl-end-capped poly(ethylene oxide). The chemical structure of the polyurethane surfactants was determined by Fourier transform infrared and ¹H-NMR, and the effects of the concentration, salt, rest time, and temperature on the surface tension were investigated. These polymeric surfactants exhibited excellent surface activity. Sample III, which was synthesized with monoallyl-end-capped poly(ethylene oxide) (number-average molecular weight = 1000), poly(propylene oxide) (number-average molecular weight = 2000), and tolylene diisocyanate, could reduce the surface tension to 37.6 mN/m at a concentration of 0.06

mol/L at 25°C. All polyurethane surfactants synthesized in this study had low critical micelle concentrations (ca. 10⁻⁴ to 10⁻⁵ mol/L) and could reduce the surface tension even at very low concentration levels. Moreover, the surface tension decreased with an increase in the temperature or the concentration of the polyurethane surfactants. The addition of salt resulted in a decrease in the surface tension, and it took some time for the polyurethane surfactants to reach a constant surface tension value. UV spectra were found to be very useful for determining the critical micelle concentration. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2956–2962, 2006

Key words: amphiphiles; polyurethanes; surfactants; synthesis; tension

INTRODUCTION

Polymeric surfactants, which contain both hydrophobic segments and hydrophilic segments, have attracted great interest in recent years because of their unique solution properties as a result of their amphiphilic molecular structure. They are among the most versatile products and have found potential applications in emulsion polymerization,^{1,2} oil enhanced recovery,³ biomedical materials,⁴ Langmuir-Blodgett (LB) films,⁵ biomimetism,⁶ and so on.

Compared with low-molecular-weight surfactants, polymeric surfactants usually have low surface activity because of their high molecular weight. Ogino et al.⁷ once pointed out that polymeric surfactants with high molecular weights generally are unable to reduce the surface tension to approximately 50 mN/m. To improve the surface activity of polymeric surfactants, some intensive research has been carried out. Baines et al.⁸ synthesized a series of diblock copolymers of

2-(dimethylamino)ethyl methacrylate and methyl methacrylate and found that the surface tension of one sample was about 45 mN/m at a concentration of 0.15 wt %. Vamvakaki et al.⁹ showed that lightly quaternized diblock copolymers of 2-(dimethylamino)ethyl methacrylate and 2-(diethylamino)ethyl methacrylate exhibited surprisingly high surface activities (37.5 mN/m), which were comparable to that found for the corresponding 2-(dimethylamino)ethyl methacrylate/2-(diethylamino)ethyl methacrylate diblock precursor (34.6 mN/m). Recently, the synthesis of diblock and triblock copolymers of ethylene oxide and ethyl acrylate by atom transfer radical polymerization was reported by Dai et al.¹⁰ The surface tension of these polymeric surfactants in aqueous solutions was about 44 mN/m. However, the results that those groups obtained were not optimistic.

In the past decade, extensive studies in academic and industrial laboratories have focused on the development of functional surfactants, especially surfactants containing unsaturated bonds. Such polymeric surfactants can be used as emulsifiers in emulsion polymerization and can copolymerize with latex, thus imparting to the latex excellent stability against high electrolyte concentrations, freeze-thaw cycling, and high shear rates. Liu et al.^{11,12} synthesized an amphiphilic poly(ethylene oxide) (PEO) macromonomer [ω -methoxypoly(ethylene oxide)₄₀undecyl α -methac-

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TABLE I
Recipe for the Preparation of Polyurethane Surfactants

Sample	TDI (mol)	F-6 (mol)	N-204 (mol)	N-210 (mol)	N-220 (mol)
I	0.1	0.1	0.1	—	—
II	0.1	0.1	—	0.1	—
III	0.1	0.1	—	—	0.1

rylate] and subsequently used it as a polymerizable surfactant in the synthesis of monodisperse polystyrene microlatexes by emulsion polymerization. Wang et al.¹³ studied the emulsion polymerization of styrene with the homopolymer of sodium dodecyl allyl sulfosuccinate as a polymeric surfactant. In recent years, much attention has also been paid to the development of hydrophobically associating polymers,^{14,15} which are of great interest for their unique rheological behaviors. However, one major difficulty in the synthesis of hydrophobically modified polymers originates from the insolubility of the hydrophobic comonomer in water. Polymerizable polymeric surfactants are helpful for solving this difficulty.

Thus, it is desirable to synthesize polymeric surfactants that have high surface activity and contain polymerizable functional groups. Because polycondensation and polyaddition reactions are generally much easier and cheaper for the preparation of block copolymers of low molecular weights (e.g., from 1000 to 50,000), we synthesized a novel series of polyurethane surfactants that contained functional polymerizable double bonds. The polyurethane surfactants that we discuss in this article can reduce the surface tension to as low as 37.6 mN/m. All three samples that we synthesized had very low critical micelle concentrations (cmc's). As discussed previously, these functional polyurethane surfactants may find potential applications in reverse emulsion polymerization and, as the hydrophobic part, in the synthesis of hydrophobically associating water-soluble polymers.

EXPERIMENTAL

Materials

Analytical-grade 2,4-toluene diisocyanate (TDI; 80%, with 2,6-toluene diisocyanate as the remainder), supplied by Shanghai Chemical Reagent Factory (Shanghai, China), was used without further purification. Industrial-grade poly(propylene oxide) {PPO; i.e., N-204 [number-average molecular weight (M_n) = 400], N-210 (M_n = 1000), and N-220 (M_n = 2000)} and monoallyl-end-capped PEO (F-6; M_n = 1000), obtained from Nanjing Jinling Oil Chemical Co. (Jiangsu, China), were dried by vacuum distillation to remove water before use. Analytical-grade dibutyltin dilaurate was purchased from Shanghai Chemical Reagent

Factory. Water used in this experiment was twice distilled and then deionized. The other chemicals used were analytical-grade and were used without further purification.

Preparation of the polyurethane surfactants

The recipe for the preparation of the nonionic polyurethane surfactants is listed in Table I. The polymerization was carried out as follows. A calculated amount of monoallyl-end-capped PEO was put into a 500-mL, four-necked flask equipped with a thermometer and a mechanical stirrer. During stirring, a calculated amount of TDI was added drop by drop to the flask. After the addition of dibutyltin dilaurate as a catalyst, the reaction was carried out at $80.0 \pm 1.0^\circ\text{C}$ for 2 h. Then, PPO (N-204, N-210, or N-220) was added to react for another 2 h at $80.0 \pm 1.0^\circ\text{C}$. After the reaction was cooled at room temperature, water was added during stirring. The reaction process is outlined in Figure 1.

Characterization

The structure of the final products was determined by Fourier transform infrared (FTIR) spectroscopy (200SXV, Nicolet, Tokyo, Japan). ¹H-NMR spectra were recorded in CDCl₃ with a Bruker Avance (300-MHz, Rheinstetten, Germany) instrument operated at room temperature. The chemical shifts were quoted in parts per million with tetramethylsilane as a reference. The UV spectra were obtained with a U-2010 spectrophotometer (Hitachi, Tokyo, Japan) at room temperature. The surface tension of the aqueous polyurethane surfactants was measured with a JZHY-180 tensiometer (Chengde Shiyangji Co., Chengde, China) with a platinum ring. The measurement accuracy was verified by the frequent measurement of the surface tension of twice distilled and deionized water (72–73 mN/m).

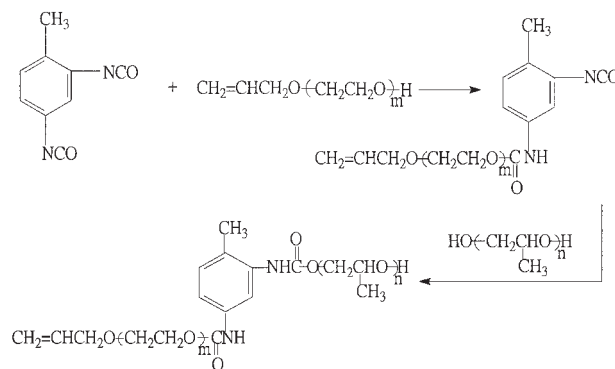


Figure 1 Synthesis of the polyurethane surfactants.

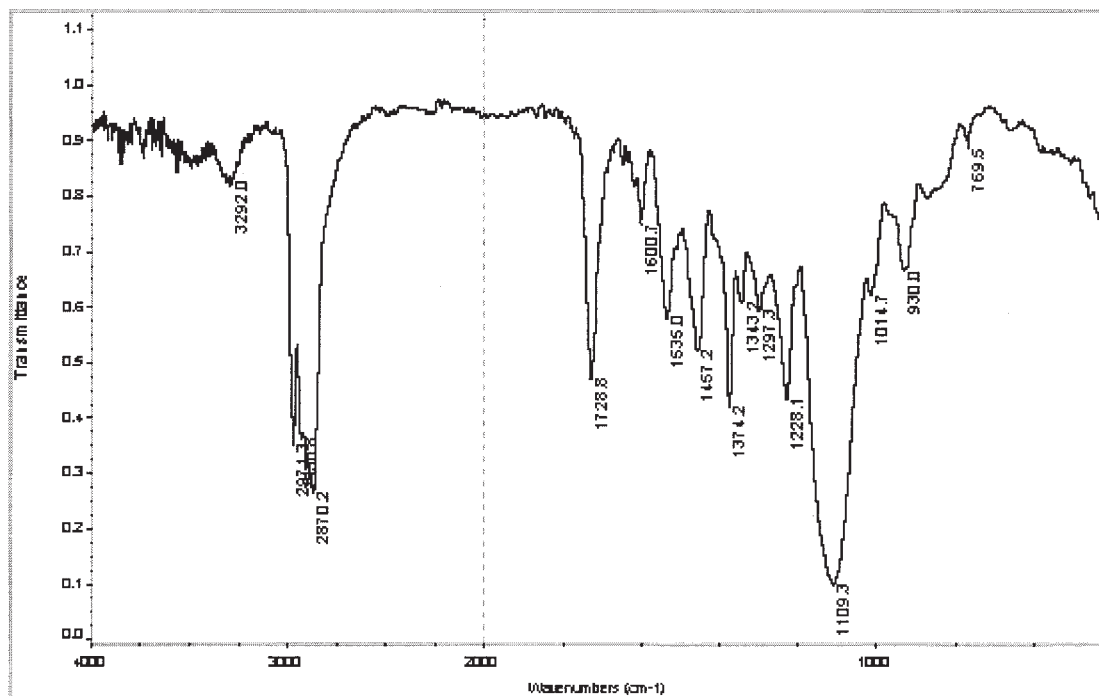


Figure 2 FTIR spectrum of sample II.

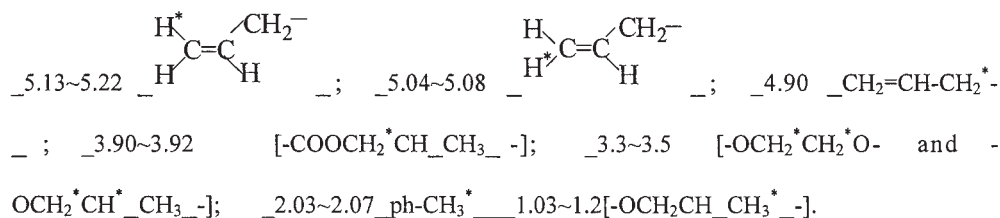
RESULTS AND DISCUSSION

Polymer characterization

The structure of the polyurethane surfactants was confirmed by FTIR and $^1\text{H-NMR}$, as shown in Figures 2 and 3, respectively. At the same time, we acquired a three-dimensional (3D) optimization of

the structure of the synthesized polyurethane surfactants by computational simulation, as shown in Figure 4.

FTIR: 3292 ($\nu_{\text{N-H}}$), 2800–3000 ($\nu_{\text{C-H}}$), 1728.8 ($\nu_{\text{C=O}}$), 1228.1 ($\nu_{\text{C-O}}$), 1600.7 ($\nu_{\text{Phenyl-H}}$), 1109.3 ($\nu_{\text{C-O-C}}$). $^1\text{H-NMR}$ (δ): 7.28–7.71 (—N—H), 6.95–7.11 (Ph—H), 5.73–5.88 ($\text{CH}_2=\text{CH}^*\text{CH}_2-$),



Effect of the concentration on the surface tension

According to Figure 5, the surface tension decreased with an increase in the concentration of the polyurethane surfactants in an aqueous solution. This trend resembles what appears in conventional low-molecular-weight surfactants, but it is noteworthy that, after the cmc was reached, the surface tension could still be reduced slightly, and there is no inflection point in the curve as known for typical surfactants. As for low-molecular-weight surfactants, the surface tension usually remains constant after the cmc is reached. Thus, this phenomenon is interesting. To the contrary, Ismail¹⁶ once synthesized a series of water-soluble poly-

urethane surfactants by the addition polymerization of TDI to poly(ethylene glycol) and/or castor oil and ethylene glycol. He found that the curve of the surface tension versus the molar concentration was just like that of classical low-molecular-weight surfactants. In other words, the surface tension was stable after the cmc was reached. The same results also occurred in the work of Shi et al.¹⁷ and Riess et al.¹⁸

The reason that the surface tension could still be reduced slightly after the cmc was reached in our work may be that the arrangements of polyurethane surfactants on the surface were not as tight as those of traditional low-molecular-weight surfactants. As

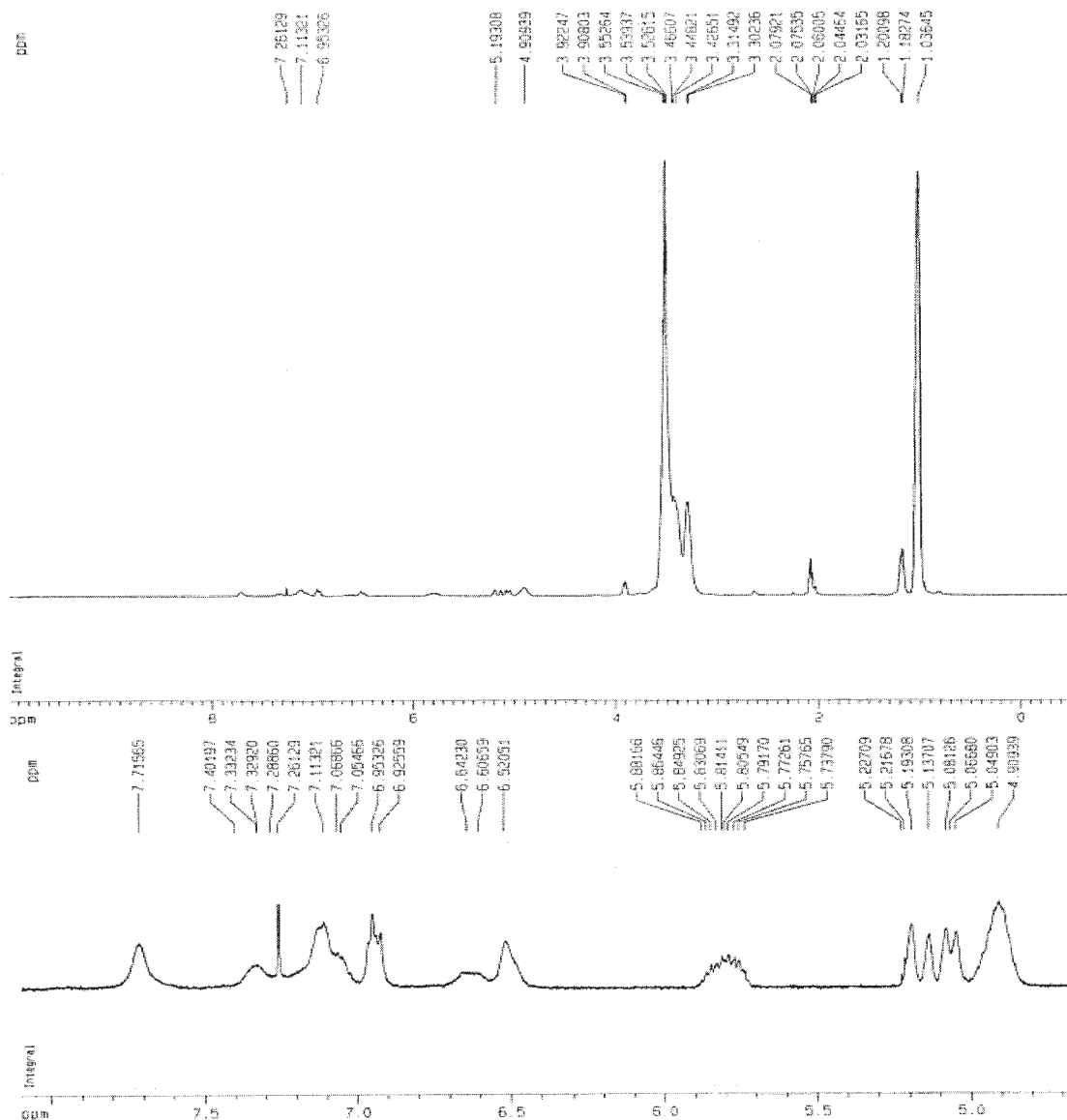


Figure 3 $^1\text{H-NMR}$ spectra of sample II.

the concentration of the polyurethane surfactants increased, the chains of the macromolecules could be condensed further. This increased the arrangement density of the hydrophobic part on the surface and resulted in the decrease of the surface tension accordingly, as the model shows in Figure 6. The curve of the surface tension versus the concentration obtained by Adler et al.¹⁹ is similar to what we obtained.

Figure 5 and Table II show that all three samples had good surface activity and very low cmc values, especially sample III, which could reduce the surface tension to as low as 37.6 mN/m. The ability to reduce the surface tension increased with an increase in the hydrophobic segment. That is, while the ratio of the hydrophobic segment increased, more hydrophobic chains were oriented on the sur-

face with their hydrophilic parts dissolved in the aqueous solution. Consequently, the surface tension was reduced.

UV spectroscopy has been widely used to determine the cmc and investigate the aggregate behaviors of surfactants.^{20–22} Figure 7 shows the UV spectra of sample II at various concentrations. On the basis of the data of Figure 7, we obtained Figure 8. A redshift occurred after sample II reached a certain concentration, and increasing the concentration made the redshift greater. This indicated that an interaction between the macromolecular chains had to exist, and after the cmc, the polyurethane surfactants could accumulate to form micelle aggregates between molecules. The cmc data given by the UV solution were approximately in agreement with what we obtained with a surface tensiometer.

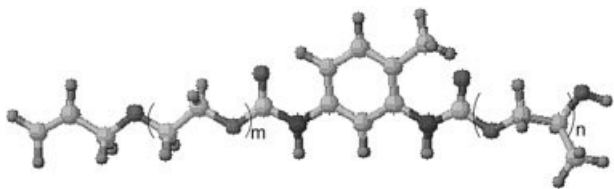


Figure 4 3D optimization of the structure of the synthesized polyurethane surfactants.

Effect of salt on the surface tension

It is widely accepted that the addition of electrolytes has an effect on the surface tension.^{23–25} As revealed by Figure 9, the addition of salt led to a slight decrease in the surface tension of sample II. This was due to the fact that the addition of salt increased the ionic strength of the aqueous solution. The hydrophilic parts of the polyurethane surfactants consisted of polyoxyethylene, whose oxygen atom could interact with H₂O or H₃O⁺ by a hydrogen bond and, consequently, was a little positive.²⁶ When the polyurethane surfactants were dissolved in water, the hydrophilic parts pointed to the water, whereas the hydrophobic parts aggregated on the surface (away from the water). As the salt was added, the repulsion between oriented hydrophobic heads and hydrophilic heads could be reduced. This resulted in a closer packaging of the surfactants on the surface and, therefore, reduced the surface tension.

The effect of salt on the surface tension reduction varied in terms of the concentration of the polyurethane surfactants. Figure 9 indicates that the effect of salt on the surface tension was more prominent at a lower concentration level. This may be attributed to the fact that macromolecular chains of the polyurethane surfactants at a lower concentration level, which could be condensed further when salt was added,

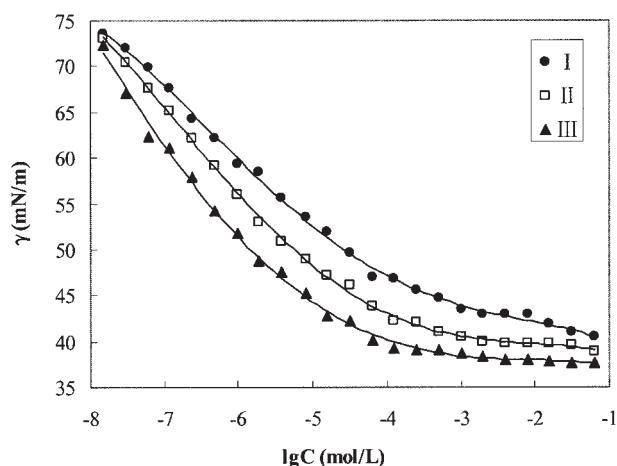


Figure 5 Curve of the surface tension (γ) versus the concentration (C) at 25°C.

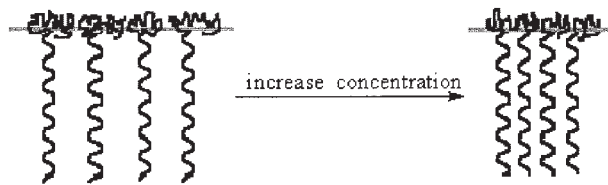


Figure 6 Schematic illustration of the decrease in the surface tension as the concentration increases after cmc.

were not arrayed as tightly as those at a higher concentration level.

Effect of the temperature on the surface tension

Figure 10 demonstrates the variation of the surface tension of sample II in aqueous solutions at 12, 18, and 25°C. The surface tension decreased with an increase in the temperature. This was due to the fact that more heat was absorbed as the temperature increased and the heat allowed enough energy for the molecules of the polyurethane surfactants to surmount the attractive forces of the interior and subsequently migrate to the surface. The enrichment of the polyurethane surfactants on the surface led to the decrease in the surface tension accordingly. Here we also can explain this phenomenon in terms of the Gibbs adsorption equation:

$$\Gamma = -\frac{d\gamma}{da} \times \frac{a}{RT}$$

where Γ is the surface excess concentration, γ is the surface tension, a is the solution activity, R is the gas constant, and T is the absolute temperature. The Gibbs adsorption equation indicates that the adsorption amount will increase with an increase in the temperature. Thus, it gives an excellent explanation for what we have discussed.

Effect of the rest time on the surface tension

In this experiment, we found that time is needed for polyurethane surfactants to reach a constant surface tension and that the time needed to obtain a constant value of the surface tension varies as the concentration of the polyurethane surfactant changes. Figure 11 shows the effect of the rest time on the surface tension of sample II with different concentrations. Accordingly, we think that it must take some time for macromolecules of polyurethane surfactants to migrate to the surface. As for polymeric surfactants, they usually have a high molecular weight, and there exist interaction and entanglement between the long macromolecular chains when they dissolve in water. The rest time

TABLE II
Data for the Final Samples

Sample	M_n	cmc (mol/L)	$\gamma_{(cmc)}$ (mN/m)	w (hydrophobic segment; %)	w (hydrophilic segment; %)
I	1574.16	6.3×10^{-5}	46.9	36	64
II	2174.16	3.2×10^{-5}	46.1	54	46
III	3174.16	1.3×10^{-5}	44.4	68	32

M_n = number-average molecular weight.

$\gamma_{(cmc)}$ = surface tension at critical micelle concentration.

w = weight percent.

allows them to adjust their conformation sufficiently and results in a better arrangement on the surface. The time needed to achieve a constant value of the surface tension for surfactants at a higher concentration level is less than that at a lower concentration level.

CONCLUSIONS

By the polycondensation of TDI with PPO and mono-allyl-end-capped PEO, we synthesized a novel series of diblock nonionic polyurethane surfactants that con-

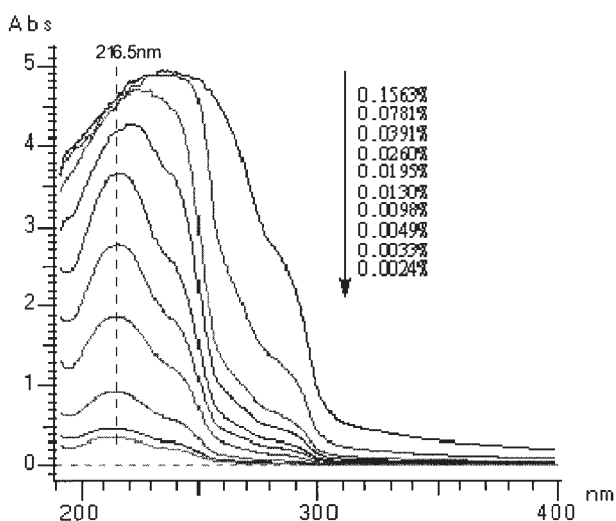


Figure 7 UV spectra of sample II at different concentrations.

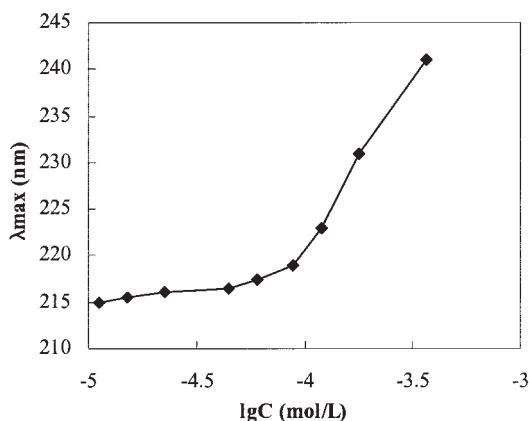


Figure 8 Curve of the maximum UV-absorbance wavelength (λ_{max}) versus the concentration (C) of sample II at 25°C.

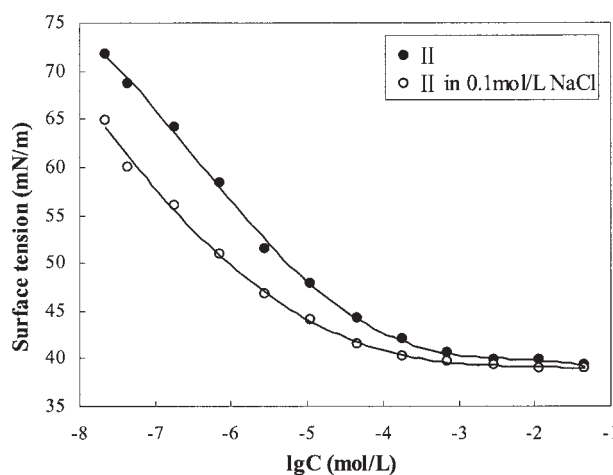


Figure 9 Effect of salt on the surface tension of sample II at 25°C. The concentration of salt in the polyurethane surfactants was kept at 0.1 mol/L.

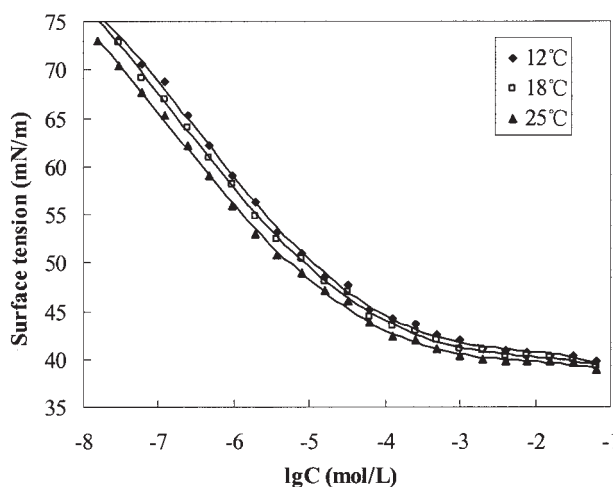


Figure 10 Curves of the surface tension versus the concentration (C) of sample II at different temperatures.

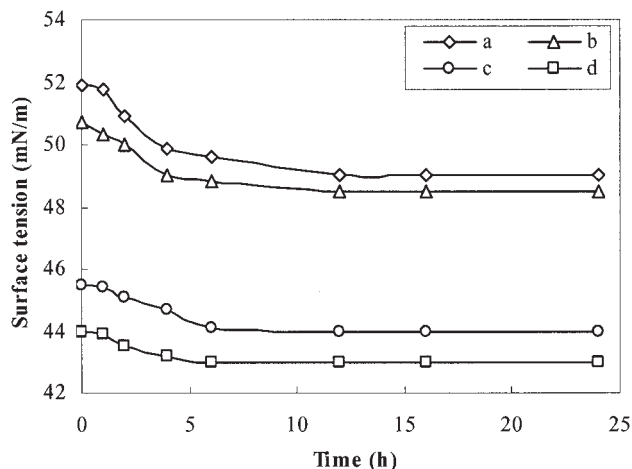


Figure 11 Effect of the rest time on the surface tension of sample II at different concentrations: (a) 0.001, (b) 0.002, (c) 0.01, and (d) 0.02 wt %.

tained reactive double bonds. All these polymeric surfactants had good surface activities; for example, sample III could reduce the surface tension to as low as 37.6 mN/m. The surface tension of these polyurethane surfactants in aqueous solutions changed as the concentration changed. An increase in the temperature was favorable for the enhancement of the surface activity, and the addition of salt led to the reduction of the surface tension. In this experiment, we also found that time was needed for the polyurethane surfactants to reach a constant value of the surface tension. These polymeric surfactants have potential applications in reverse emulsion polymerization as promising alternatives to conventional low-molecular-weight surfactants. At the same time, they can incorporate with hydrophilic chains as the hydrophobic part in the synthesis of hydrophobically associating water-soluble polymers. Further studies in this direction are currently in progress.

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