



Synthesis and properties of cocotriethoxylpropanediamine oxide

Hongmao Fu, Yunling Li, Yongbo Song & Jun Li

To cite this article: Hongmao Fu, Yunling Li, Yongbo Song & Jun Li (2017) Synthesis and properties of cocotriethoxylpropanediamine oxide, Journal of Dispersion Science and Technology, 38:10, 1421-1426, DOI: [10.1080/01932691.2016.1250217](https://doi.org/10.1080/01932691.2016.1250217)

To link to this article: <https://doi.org/10.1080/01932691.2016.1250217>



© 2018 Taylor & Francis Group, LLC



Published online: 15 Mar 2017.



Submit your article to this journal [↗](#)



Article views: 603



View related articles [↗](#)



View Crossmark data [↗](#)



Citing articles: 2 View citing articles [↗](#)

Synthesis and properties of cocotriethoxypropanediamine oxide

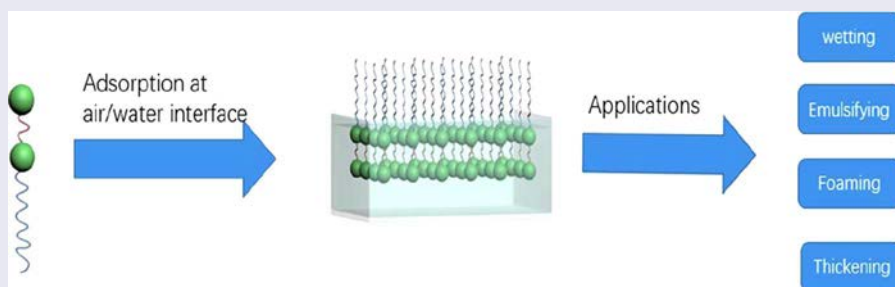
Hongmao Fu, Yunling Li, Yongbo Song, and Jun Li

China Research Institute of Daily Chemical Industry, Taiyuan, China

ABSTRACT

A new kind of amine oxide surfactant – cocotriethoxypropanediamine oxide (CTPDAO) – was synthesized by a two-step process. The molecular structure was characterized by FTIR spectra and ^1H NMR. The new surfactant showed high surface activity in aqueous solution in the surface tension measurement. Emulsifying capacity and wetting ability were studied in comparison to dodecylmethylamine oxide (DDMAO). The results indicate that this new surfactant could reach the lowest surface tension of 30.4 mN m^{-1} in aqueous solution with a critical micelle concentration (CMC) of 0.23 mmol L^{-1} . The wetting ability of DDMAO is better than that of CTPDAO. Compared with CTPDAO, DDMAO shows a greater capacity to emulsify soybean oil, although CTPDAO is a better emulsifying agent for liquid paraffin. The foaming properties and thickening function of DDMAO and CTPDAO mixed with alcohol ether sulfate (AES) and dodecylbenzene sulfonate (LAS) were also investigated. The results show that CTPDAO is a superior foam stabilizer than DDMAO while CTPDAO and DDMAO both have excellent thickening functions.

GRAPHICAL ABSTRACT



ARTICLE HISTORY

Received 22 September 2016
Accepted 16 October 2016

KEYWORDS

Amine oxide; foaming properties; surface activity; synthesis; wetting

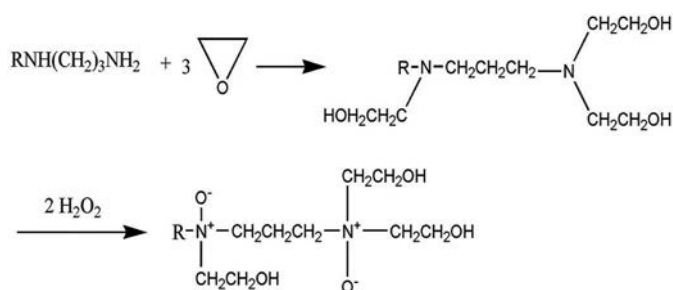
1. Introduction

Amine oxides are multifunctional inorganic surface active agents.^[1] The alkalinity of amine oxides makes them demonstrate nonionic behaviors in neutral or alkaline solution, and show cationic characteristics in acid solution.^[2] Amine oxides have been known to have excellent surface activity and antistatic characteristics for long.^[3] They exhibit excellent emulsifying, wetting, foaming, and thickening properties. Amine oxides are often used in shampoos, detergents, and textile auxiliary agents because of their multiple functions.^[4–6] Amine oxides are usually compatible with anionic surfactants. They show great synergistic effects when mixed with common anionic surfactants and provide more desirable properties than single surfactants.^[7,8] And for this reason, amine oxides are usually mixed with other surfactants to investigate the synergistic effects.

Dodecylmethylamine oxide (DDMAO) is an amine oxide surfactant that is widely used and has been studied in-depth recently.^[9,10] Mixtures of DDMAO and sodium dodecylsulfate

(SDS) or dodecyltrimethyl ammonium bromide (DTAB) show excellent synergistic effects. Hydroxyl groups are common hydrophilic groups and are usually connected to surfactant molecules to obtain superior properties. Amine oxides containing hydroxyl groups often show advantageous properties such as a better water solubility, low CMC, compatibility with other surfactants, and so on.^[11] Diamine oxide, which contains two N-O bonds, has excellent surface properties as well. Although it has not been researched too much, it is of great potential application in the future.

In this article, cocotriethoxypropanediamine oxide (CTPDAO) containing hydroxyethyl groups was synthesized by a two-step process as shown in Scheme 1. The surface activity of CTPDAO was investigated. Meanwhile, the wetting ability and emulsifying capacity were measured in comparison to DDMAO. The foaming properties and thickening function of CTPDAO and DDMAO mixed with sodium alcohol ether sulfate (AES) and dodecylbenzene sulfonate (LAS) were also studied.



Scheme 1. Synthesis route of cocotriethoxypropanediamine oxide.

2. Experimental

2.1. Materials and instruments

2.1.1. Chemicals and materials

The raw material cocopropanediamine (CPDA) was purchased from Tianpu Chemical Co., Ltd. AES and LAS were from China Research Institute of Daily Chemical Industry. Hydrogen peroxide (30 wt%) and liquid paraffin were purchased from Tianjin University Chemical Reagents Co. Petroleum ether (60–90) and diethyl ether were of analytical reagent grade (A.R.) and purchased from Tianjin University Chemical Experiment Plant and Tianjin Kemiou chemical reagent Co., Ltd.

2.1.2. Experimental techniques

The FTIR spectrum was recorded on a Bruker Vertex 70 FTIR spectrometer (Germany). ^1H NMR spectra were detected by a Varian Inova-400 spectrometer (USA). Surface activity was measured using a Krüss K12 Processor Tensiometer. Viscosities were measured using a NDJ-79 rotating viscometer. Foaming properties were measured using a Modified Ross-Miles apparatus.

2.2. Synthesis of CTPDAO

CTPDAO was synthesized by integrating two traditional synthetic processes, which were known as ethoxylation and quaternization reaction. Scheme 1 shows the two-step reaction process and the molecular structures of the whole synthesis route.

For the first step, 256 g CPDA was added to the autoclave, then heated to 110°C with the pressure being 0.4 MPa. A total of 44 g ethylene oxide was then added to the autoclave for several times to keep the pressure no greater than 0.4 MPa. The reaction was operated under 110–120°C for one and a half hours to obtain the medium product cocotriethoxypropanediamine (CTPDA).

For the second step, 27.5 g CTPDA dissolved in 33.3 ml water was added to a four-necked flask. A total of 19.6 g hydrogen peroxide (diluted to 15 wt%) was then added into the flask at 65–70°C range for 30–40 minutes. Then the four-necked flask was heated to 80°C. The reaction was maintained at 80°C for 4 hours to obtain the CTPDAO aqueous solution. The whole process should be kept stirring. The active content of the product was about 25 wt%.

To obtain purified CTPDAO, a mixture of petroleum ether (volume fraction 90%) and ethyl acetate (volume fraction 10%)

was used as the oil phase, whereas the CTPDAO solution was engaged as the aqueous phase to extract impurities, mostly tertiary amine unreacted, from the water phase to increase the content of CTPDAO in the aqueous solution.^[12] Every 10 g crude aqueous product was manipulated each unit extraction, with 20 mL petroleum ether/ethyl acetate mixture. The aqueous phase, which contained a substantial amount of the CTPDAO product, was then evaporated with a rotary-evaporator to remove the water. Then the sample was dried in a thermostatic vacuum drier at 65°C for 48 hours to obtain yellow viscous liquids with high purity, which was higher than 92 wt%.

2.3. Properties measurement

2.3.1. Surface activity

The surface tensions of CTPDAO were measured at 25°C \pm 0.2°C from a series of aqueous solutions with a platinum ring tensiometer shown in Figure 3. The surface tension of double-distilled water, 72.0 \pm 0.3 mN m⁻¹, was used for calibration purposes. Surfactant solutions were prepared with double-distilled water. Every sample was stabilized for 10 minutes before measurement.

2.3.2. Wetting ability

The wetting ability of CTPDAO was measured through the canvas descending method at room temperature.^[13] In a 1000 ml beaker, a canvas disk was immersed in aqueous solution rapidly. Then, keep the time until the disk started to sink because it was fully permeated by the solution. Every single solution was measured five times to obtain the average wetting time. The wetting ability is obtained from this period of wetting time recorded and it is in negative correlation with the wetting time.

2.3.3. Emulsifying capacity

Emulsifying test was carried out in a glass cylinder of 100 ml at room temperature.^[14] A total of 40 ml of liquid paraffin or soybean oil and 40 ml of CTPDAO solution were added to a 100 ml cylinder together and shaken up and down vigorously five times every minute. Then the cylinder was kept still to record the time of 10 ml water separated from the emulsion. The whole process was operated five times and the emulsifying capacity was determined by the average time for the separation of 10 ml water. The longer time it takes to separate 10 ml water, the better emulsifying capacity the surfactant shows.

2.3.4. Foaming properties

The foaming properties were tested using the Modified Ross-Miles method at 50°C.^[15] First, 50 ml surfactant solution of 2.5 g/l was poured into the bottom of a flask. Then, 500 ml of the solution in a funnel was placed into the flask from the top of the apparatus. After the solution had run out of the funnel, the time and foam volume were recorded at 30 seconds, 5 minutes, and 10 minutes. Foaming ability was determined by the foam volume after 30 seconds. Foam stability was determined by comparing the foam volumes after 10 minutes and 30 seconds in the Ross-Miles apparatus.

2.3.5. Thickening function

The viscosity measurements of CTPDAO/AES, CTPDAO/LAS, DDMAO/AES, and DDMAO/LAS complex systems with a total active content of 20 wt% were operated using an NDJ-79 rotating viscometer at 25°C. The higher the viscosity, the better is the thickening function.

3. Results and discussion

3.1. Structure characterization

In order to verify the molecular structure of CTPDAO, FTIR and ^1H NMR were performed. The results are shown in Figures 1 and 2. The IR spectra of CTPDAO showed absorption bands at 3282 cm^{-1} (O-H stretching), 2924 , 2852 cm^{-1} (C-H stretching), 1466 cm^{-1} (C-H bending), 1124 cm^{-1} (C-N stretching), 1076 cm^{-1} (C-O stretching), and 721 cm^{-1} (C-H rocking). The FTIR spectra correspond well with the molecular structure of CTPDAO. The ^1H NMR spectra of CTPDAO showed peaks at 0.89 ppm (t, 3H, $\text{CH}_3\text{-(CH}_2)_7\text{-CH}_2\text{-CH}_2\text{-N}$), 1.27 ppm (d, 14H, $\text{CH}_3\text{-(CH}_2)_7\text{-CH}_2\text{-CH}_2\text{-N}$), 1.50 ppm (s, 2H, $\text{CH}_3\text{-(CH}_2)_7\text{-CH}_2\text{-CH}_2\text{-N}$), 1.72 ppm (t, 2H, $\text{CH}_3\text{-(CH}_2)_7\text{-CH}_2\text{-CH}_2\text{-N-CH}_2\text{-CH}_2\text{-N}$), 2.70 ppm (t, 8H, $\text{CH}_3\text{-(CH}_2)_7\text{-CH}_2\text{-CH}_2\text{-N-(CH}_2\text{CH}_2\text{OH)-CH}_2\text{-CH}_2\text{-CH}_2\text{-N-(CH}_2\text{CH}_2\text{OH)}_2$), 3.58 ppm (t, 4H, $\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-N}$), and 3.74 ppm (t, 6H, $\text{N-(CH}_2\text{CH}_2\text{OH)-CH}_2\text{-CH}_2\text{-CH}_2\text{-N-(CH}_2\text{CH}_2\text{OH)}_2$). Besides, the solvent peak of CDCl_3 appeared at 7.29. It should be stated that the doubles at 2.70 and 3.74 ppm are derived from the coupling of the H atom on the adjacent methylidyne, which could be explained by the fact that the synthesized molecule is consistent with CTPDAO. Moreover, the other impacts of the spectrum, such as the intensity and the methylidyne, are in good accordance with the new amine oxide product CTPDAO just as we designed. In general, the molecular structure of CTPDAO could be well confirmed by FTIR and ^1H NMR and the synthesized material was the target material we designed.

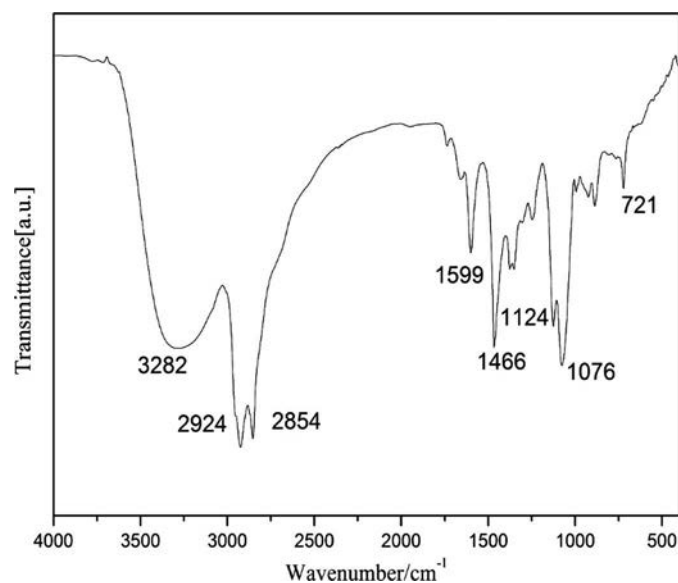


Figure 1. FTIR spectrum of CTPDAO.

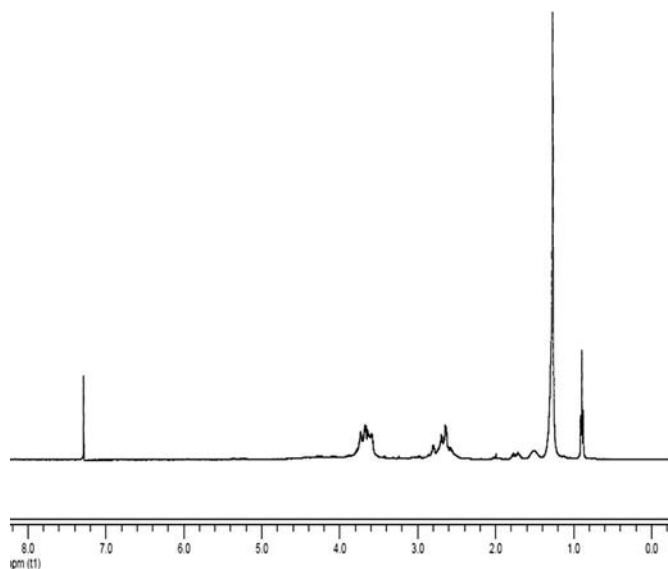


Figure 2. ^1H NMR spectrum of CTPDAO.

3.2. Surface activity

Surface activity is the key property of a surfactant, and it is defined as the ability and efficiency to decrease the surface tension of aqueous solution. The surface tension decreased with the increasing surfactant concentration and had a break point at a certain concentration, which is known as the critical micelle concentration (CMC). The CMC and γ_{CMC} of CTPDAO were determined from the linear fitting results of the plot shown in Figure 3. According to the linear fitting results of the surface tension curve, the surface excess concentrations of CTPDAO (Γ_{max}) and the minimum surface area per surfactant molecule (A_{min}) were calculated from the Gibbs adsorption equation.

$$\Gamma_{\text{max}} = -\frac{1}{2.303nRT} \left(\frac{\partial \gamma}{\partial \log C} \right)_T \quad [1]$$

$$A_{\text{min}} = \frac{1}{N_A \Gamma_{\text{max}}} \quad [2]$$

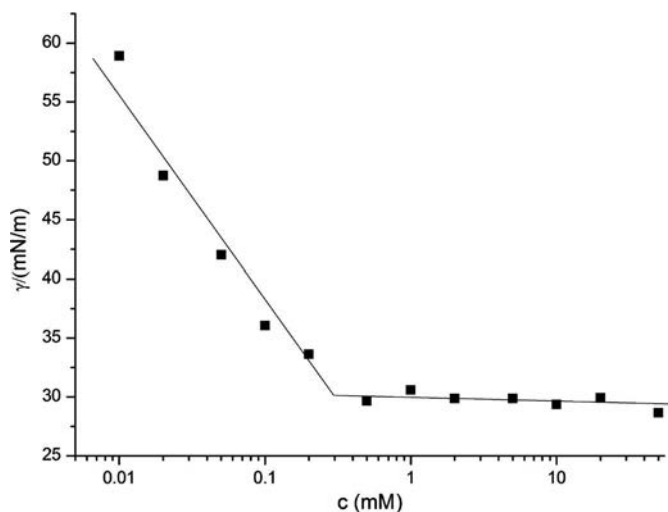


Figure 3. Surface tension versus concentration for CTPDAO at 25°C.

Table 1. Surface properties of CTPDAO.

Surfactant	CMC(mM)	γ_{CMC} (mN/m)	r_{max} ($\mu\text{mol}/\text{m}^2$)	Amin (\AA^2)	pC_{20}
CTPDAO	0.23	30.40	3.36	49.39	4.72
DDMAO ^a	0.75	23.9	4.97	33.4	4.17

^aFrom Ref.^[17]

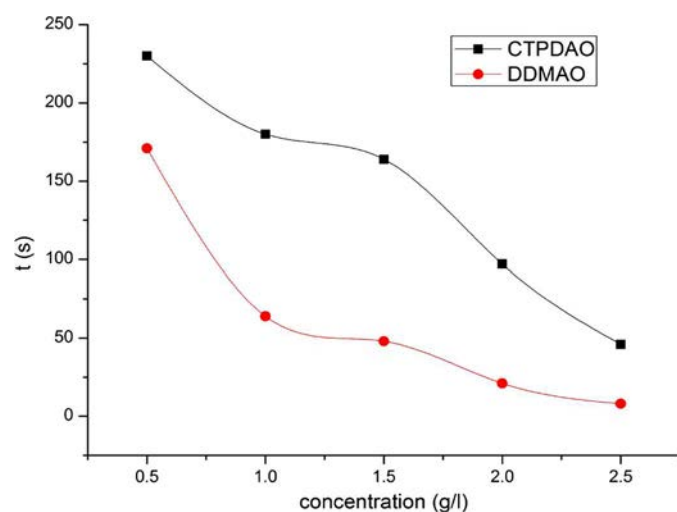
Here, R is the gas constant, T is the absolute temperature, N_A is Avogadro's number, and C is the concentration of the surfactant solution. The adsorption of surfactants can be expressed by the pC_{20} value. The larger the pC_{20} value, the higher is the adsorption efficiency of the surfactant.^[16]

The surface activity parameters are shown in Table 1. As expected, CTPDAO could reach the lowest aqueous surface tension of 30.4 mN m^{-1} . The CMC is 0.23 mmol L^{-1} . Compared with DDMAO, whose γ_{CMC} is 23.9 mN m^{-1} with the CMC being 0.75 mmol L^{-1} , CTPDAO has a lower CMC and a higher γ_{CMC} . In addition, CTPDAO has a larger pC_{20} value than DDMAO.^[17]

We speculate that these superior features of this new surfactant can be attributed to the existence of three hydroxyl groups and two N-O bonds. Hydroxyethyl groups can provide a much higher steric hindrance than the methyl groups. Meanwhile, CTPDAO has a better solubility. The larger pC_{20} value indicates that CTPDAO is more easily adsorbed than DDMAO. This is because the hydroxyl groups of CTPDAO can form hydrogen bonds more easily with water. In summary, CTPDAO has excellent surface activity according to the surface tension measurement.

3.3. Wetting ability

Wetting ability is a significant property of a surfactant and is therefore worth determining. As shown in Figure 4, the wetting times of CTPDAO and DDMAO at different concentrations were recorded. It could be learned that when surfactants wet the canvas fiber, it will form a three-phase interface of "solid-liquid-gas." When added to solution, surfactant molecules will be adsorbed at the interface of "solid-liquid" more than that the interface of "liquid-gas".

**Figure 4.** Wetting times with different concentrations of CTPDAO and DDMAO.

The more the surfactants adsorbed on the solid surface, the stronger the wetting ability is on the canvas.^[18] The results indicate that the wetting ability of DDMAO is much higher than that of CTPDAO.

3.4. Emulsifying capacity

Emulsifying capacity is of great value in many application processes. The emulsifying capacities of CTPDAO and DDMAO for soybean oil and liquid paraffin were measured in a graduated cylinder with a glass stopper at room temperature. The time for the separation of 10 ml of water was taken as an estimate of the emulsifying capacity. Figure 5 shows the results of the emulsifying capacity of CTPDAO and DDMAO to emulsify soybean oil and liquid paraffin, respectively. As the concentration increased, the emulsion time for both CTPDAO and DDMAO showed a regular increasing stability. The capacity of CTPDAO and DDMAO to emulsify soybean oil was better than that of liquid paraffin based on the longer emulsifying time. Meanwhile, CTPDAO showed a greater capability to emulsify soybean and a slightly better capability to emulsify liquid paraffin than DDMAO. It can be concluded that CTPDAO exhibited superior properties in the emulsifying capability test than normal amine oxide product DDMAO and demonstrated the potential to be a better emulsifying agent.

3.5. Foaming properties

Foaming is a significant application of common surfactants that contain two major parts: foamability and foam stability. The foaming properties of different mass compositions of CTPDAO/AES, CTPDAO/LAS, DDMAO/AES, and DDMAO/LAS complex systems with a total concentration of 2.5 g/l were measured using the Modified Ross-Miles method at 50°C . The foaming ability is defined as the foam volume at 30 seconds and the foam stability is expressed by the ratio of the foam volumes after 10 minutes and 30 seconds. Table 2 shows the foamability and foam stability of four complex systems with different weight proportions. For single

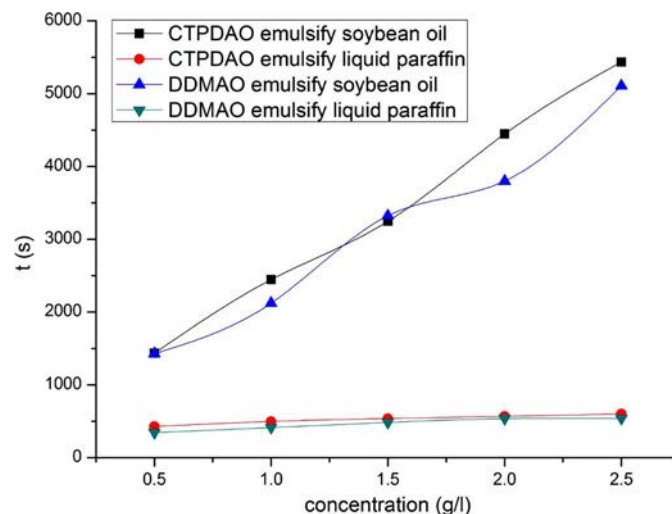
**Figure 5.** The emulsifying capacities of CTPDAO and DDMAO for soybean oil and liquid paraffin.

Table 2. Foamability and foam stability of samples.

Surfactant (weight proportion)	The volume of foam			Surfactant (weight proportion)	The volume of foam		
	30 seconds	10 minutes	V_{10min}/V_{30s}		30 seconds	10 minutes	V_{10min}/V_{30s}
CTPDAO/AES				CTPDAO/LAS			
0:1	330	90	0.27	0:1	250	100	0.25
1:20	340	270	0.79	1:20	390	355	0.91
1:15	350	280	0.8	1:15	400	245	0.61
1:10	385	305	0.79	1:10	420	290	0.69
1:5	415	335	0.81	1:5	445	340	0.76
1:0	480	210	0.44	1:0	480	210	0.44
DDMAO/AES				DDMAO/LAS			
0:1	330	90	0.27	0:1	250	100	0.25
1:20	390	350	0.90	1:20	425	260	0.62
1:15	430	395	0.92	1:15	440	270	0.61
1:10	440	410	0.93	1:10	485	290	0.60
1:5	475	445	0.94	1:5	515	350	0.68
1:0	520	270	0.52	1:0	520	270	0.52

Table 3. The viscosity of mixed surfactant systems.

Amine oxide (wt%)	The viscosity of CTPDAO/AES mixed surfactants (mPa-s)	The viscosity of CTPDAO/LAS mixed surfactants (mPa-s)	The viscosity of DDMAO/AES mixed surfactants (mPa-s)	The viscosity of DDMAO/LAS mixed surfactants (mPa-s)
0	11	380	11	380
5	12	2500	3400	1250
10	11	1200	1800	1300
15	12	18	180	360
20	12	12	13	13

surfactants, the foamability and foam stability of CTPDAO are slightly higher than DDMAO, much higher than AES and LAS. For the four complex systems, with the increase of the proportion of amine oxide, the foamability increases; the foam stability of the complex system is higher than that of the single surfactant due to synergistic effect; the foamability and foam stability of the two complex systems with LAS are better than that those with AES. At the same weight proportion, the foamability and foam stability of DDMAO/AES are better than those of CTPDAO/AES, whereas the foamability and foam stability of CTPDAO/LAS are better than those of DDMAO/LAS. The results indicate that CTPDAO demonstrates excellent synergetic effects when mixed with AES and LAS in the foaming test, which is better than that of DDMAO. Owing to the ethoxyl groups, CTPDAO has better solubility and shows excellent promise in mixtures with other surfactants.

3.6. Thickening function

Amine oxides surfactants are generally excellent thickeners and for this reason are usually added to shampoos. This thickening function of CTPDAO was studied by a rotating viscometer. The viscosities of CTPDAO/AES, CTPDAO/LAS, DDMAO/AES, and DDMAO/LAS complex systems are shown in Table 3. CTPDAO had no thickening function to AES, which was odd. We could just see it as an exception. From the data, it is seen that CTPDAO has similar viscosity to AES. When amine oxide/AES = 1:9, the mixture system is gentle and shows excellent thickening function.^[19] We can speculate that the total active content and amine proportion of the mixture solution do not correspond to the range that CTPDAO/AES exhibits thickening function. For the CTPDAO/LAS and DDMAO/AES mixed systems, the

maximum viscosity was achieved in the amine oxide content proportion of 5 wt%, while it was 10 wt% for the DDMAO/LAS complex system.

4. Conclusions

CTPDAO was synthesized through a two-step process, which was characterized by ¹H NMR and IR spectra. CTPDAO has excellent surface activity, which can lower the surface tension to 30.40 mN m⁻¹. Among the two amine oxides, DDMAO has a better wetting activity than CTPDAO. Meanwhile, compared with DDMAO, the emulsifying capacity of CTPDAO for liquid paraffin is superior. However, the emulsifying capacity of DDMAO for soybean oil is better than that of CTPDAO. For complex surfactant systems with AES and LAS, the foamability and foam stability improved because of the existence of CTPDAO or DDMAO. The maximum viscosities of DDMAO/AES, CTPDAO/LAS, and DDMAO/LAS mixed surfactant systems were achieved at 5 wt% and 10 wt% amine oxide concentration, whereas the viscosity of CTPDAO/AES has no maximum viscosity. In general, CTPDAO is an excellent foam stabilizer and thickener and it holds great promise for future application for its excellent surface properties in aqueous solution.

Funding

The authors acknowledge the financial support of the National Science and Technology Support Project of China (No. 2014BAE03B03).

References

- [1] Fang, L. and Xia, G. (2015) *Deterg. Cosmet.*, 38: 22–24.
- [2] Guenther, F. and K. (1939) U.S. Patent 2: 169,976.

- [3] Hui Zhanga, Clarence A. Millera*, Peter R. Garrettb, and Kirk H. Raneyc. (2005) *J. Surf. Deterg.*, 8: 99–107.
- [4] Zhang, H., Miller, C.A., Garrett, P.R., and Raney, K.H. (2005) *J. Surf. Deterg.*, 8: 99–107.
- [5] Lim, J.C. and Han, D.S. (2011) *Colloids Surf. A.*, 389: 166–174.
- [6] Singh, S.K., Bajpai, M., and Tyagi, V.K. (2006) *J. Oleo. Sci.*, 55: 99–119.
- [7] Varade, D., Joshi, T., Aswal, V.K., Goyal, P.S., Hassan, P.A., and Bahadur, P. (2005) *Colloids Surf. A.*, 259: 103–109.
- [8] Abdel-Rahem, R.A. (2012) *J. Chem. Eng. Data*, 57: 957–966.
- [9] Garcia, M.T., Campos, E., and Ribosa, I. (2007) *Chemosphere*, 69: 1574–1578.
- [10] Kakehashi, R., Yamamura, S., Tokai, N., Takeda, T., Kaneda, K., Yoshinaga, K., and Maeda, H. (2001) *J. Colloid Interface Sci.*, 243: 233–240.
- [11] Li, H. and Wang, X. (2008) *Sens. Actuat. B. Chem.*, 134: 238–244.
- [12] Yongjie Zhang, Xia Xin, Jinglin Shen, Weiyue Tang, Yingjie Ren, and Lin Wang. (2014) *Adv*, 4: 62262–62271.
- [13] Mao, P. (1988) *The Publishing House of Light Industry*. Peking. 456–462.
- [14] Yongjie Zhang, Yunling Li, Yongbo Song, and Jun Li. (2016) *Colloid Polym. Sci.*, 294: 271–279.
- [15] Wang, G.Y., Du, Z.P., Zhang, W., and Cao, Q.Y. (2009) *Tenside Surf. Deterg.*, 46: 214–217.
- [16] Yongjie Zhang, Yunling Li, Yongbo Song, and Jun Li. (2015) *RSC Adv.*, 5: 105952.
- [17] Ruitao Wang, Yunling Li, and Qiuxiao Li. (2013) *J. Surf. Deterg.*, 16: 509–514.
- [18] Xu, Q., Wang, L., and Xing, F. (2011) *J. Surf. Deterg.*, 14: 85–90.
- [19] Ping Li, Li Li, and Xu Yang (2005) *Deterg. Cosmet.*, 282: 19–22.