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ORIGINAL ARTICLE

Synthesis and Properties of Dodecyldiethoxylamine Oxide

Ruitao Wang · Yunling Li · Qiuxiao Li

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Abstract Dodecyldiethoxylamine oxide (DDEAO) was synthesized by the reaction of dodecyldiethoxylamine with hydrogen peroxide in water as the solvent. Surface activity, wetting ability and emulsifying capacity were investigated and compared with that of dodecyldimethylamine oxide (DDMAO). Results indicate that the critical micelle concentration (CMC) of DDEAO is lower than that of DDMAO, while its surface tension at CMC (γ_{CMC}) is slightly higher. The wetting ability of DDEAO is similar to that of DDMAO. For its capacity of emulsifying liquid paraffin, DDEAO is found to be better than DDMAO, but it is the opposite for emulsifying soybean oil. The foaming properties and thickening function of DDEAO in mixtures with alcohol ether sulfate and alkylbenzene sulfonate were also studied. As expected, complex surfactant systems exhibit good foaming ability and DDEAO exhibits a good thickening function.

Keywords Amine oxide · Synthesis · Surface activity · Properties

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R. Wang · Y. Li (✉) · Q. Li
China Research Institute of Daily Chemical Industry,
34# Wenyuan Str., Taiyuan 030001, Shanxi Province,
People's Republic of China
e-mail: lyunl0068@sina.com

Introduction

Amine oxide surfactants show nonionic characteristic in neutral or alkaline solution, and demonstrate cationic behavior in acid solution. They show less irritation to the skin, high foaming properties and an excellent thickening function [1–3]. These surfactants are widely used in detergents, shampoos, cosmetics and textile auxiliaries based on their characteristics and advantages [2, 3]. Surfactant mixtures often behave synergistically and provide more desirable properties than single surfactants [4–7]. So amine oxides are usually used together with other surfactants.

Among amine oxides, dodecyldimethylamine oxide (DDMAO) is the most widely used surfactant and has been extensively researched [8–10]. Mixtures of DDMAO and sodium dodecylsulfate (SDS) or dodecyltrimethyl ammonium bromide (DTAB) have been widely studied. Results reported have shown good synergistic effects of mixed solutions [11, 12]. Hydroxyl groups connected to surfactant molecules often show advantageous properties such as a better water-solubility, low CMC, highly favorable compatibility with other surfactants and so on [13]. Consequently, amine oxide surfactants containing hydroxyl groups not only retain the superior performance of amine oxide, but also can achieve more than the expected performance.

In this paper, dodecyldiethoxylamine oxide (DDEAO) containing hydroxyl groups was synthesized. The synthesis route and chemical structure are shown in Scheme 1. The pH of DDEAO (the weight concentration is 1 %) is 6.0 in aqueous media. The surface activity, wetting ability and emulsifying capacity of DDEAO were investigated and compared to those of dodecyldimethylamine oxide. The foaming properties and the thickening function of DDEAO

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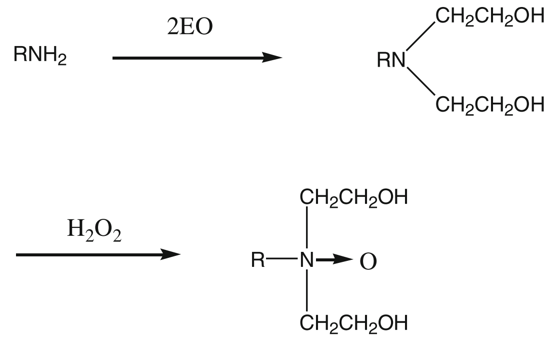

Scheme 1 Synthesis route of dodecyldiethoxylamine oxide

mixed with alcohol ether sulfate and alkyl benzene sulfonate in complex systems were also measured.

Experimental

Materials and Instruments

Dodecyldiethoxylamine was synthesized from dodecanamine and ethylene oxide. Dodecyldimethylamine oxide, sodium alcohol ether sulfate (AES) and dodecylbenzenesulfonate (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.

Surface activity was studied using a Krüss K12 Processor Tensiometer. Foaming properties were measured using a Ross-Miles apparatus. Viscosities were measured using a NDJ-79 rotating viscometer.

Synthesis of DDEAO

In a four-necked flask, 0.1 mol dodecyldiethoxylamine was put into 27.5 ml water. Then, 0.12 mol hydrogen peroxide (diluted to 10 wt%) was added dropwise into the four-necked flask at 75–80 °C for 40–60 min with continuous stirred. The reaction was maintained for 4 h at 80–85 °C. The active content was about 30 wt%. The molecular structures of DDEAO were characterized by IR (FTLA200-104, Boman, Canada) and ^{1}H NMR (Avance III 400 MHz, Bruker, USA). IR spectra of DDEAO showed absorption bands at 3,274, 3,385 cm^{-1} (–OH stretching), 2,919, 2,851 cm^{-1} (C–H stretching), 1,467 cm^{-1} (C–H bending), 1,075 cm^{-1} (C–N stretching), 1,047 cm^{-1} (C–O stretching), and 726 cm^{-1} (C–H rocking). ^{1}H NMR ($CDCl_3$, ppm): δ 0.87 (t, 3H, $\mathit{CH_3}$–$(CH_2)_9$–CH_2–CH_2–N), 1.25 (d, 18H, CH_3–$(\mathit{CH_2})_9$–CH_2–CH_2–N), 1.63 (s, 2H, CH_3–$(CH_2)_9$–$\mathit{CH_2}$–CH_2–N), 3.32 (m, 2H, CH_3–$(CH_2)_9$–CH_2–$\mathit{CH_2}$–N), 3.47 (m, 4H, HO–CH_2–$\mathit{CH_2}$–N–$\mathit{CH_2}$–CH_2–OH), 4.06 (m, 4H, 2×–CH_2–$\mathit{CH_2}$–OH), 4.26–5.31 (s, 2H, 2×–CH_2–CH_2–*OH*).

Measurement of Properties

Surface Activity

The surface tensions of the DDEAO and DDMAO were measured at 25 ± 0.2 °C from a series of aqueous solutions with a platinum ring tensiometer. The surface tension of double-distilled water, 72.0 ± 0.3 mN/m, was used for the calibration purposes. Surfactant solutions were prepared with the double-distilled water. The samples were stabilized for 10 min in the instrument before measurements were taken.

Wetting Ability

The wetting ability was measured according to the canvas descending method [14]. A canvas disk was immersed in surfactant solution at room temperature, after some time, the disk was permeated by surfactant solution and started to sink. The wetting ability is determined by this period from immersion to sinking. The shorter the wetting time, the better is the wetting ability. The wetting ability was determined as the average value from five measurements.

Emulsifying Capacity

Emulsifying capacity was measured in a 100-ml glass cylinder with a stopper at room temperature [15]. First, 40 ml of liquid paraffin or soybean oil and then 40 ml of a series of surfactant solutions at different concentrations was poured into a 100-ml cylinder. The stopper was placed in the cylinder, and it was shaken up and down five times then left to stand for 1 min. The experiment was repeated five times, and the time for the separation of 10 ml water was the emulsifying capacity. The longer the time for the separation of 10 ml water, the better is the emulsifying capacity.

Foaming Properties

The foaming properties were measured by the Ross-Miles method at 50 °C [16]. A 50-ml sample of 2.5 g/l surfactant solution was placed in the bottom of a flask and 500 ml of the same solution in a funnel was allowed to fall into the flask from the top. After solution had run out of the funnel, the time and foam volume were recorded at 30 s, 5 and 10 min. Foaming ability was determined by the foam volume after 30 s. Foam stability was determined by comparing the foam volumes after 10 min and 30 s in the Ross-Miles apparatus.

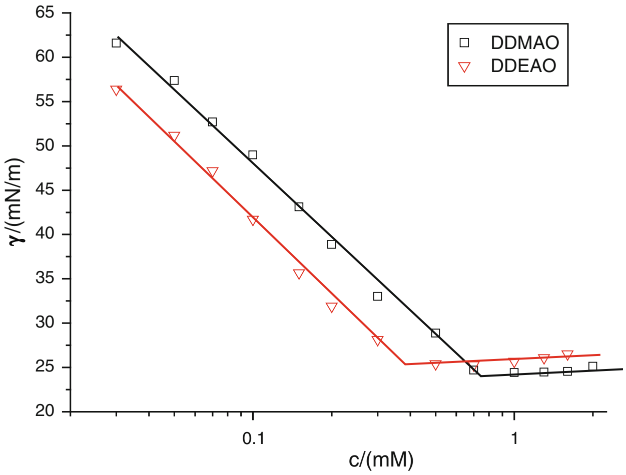

Fig. 1 Surface tension versus concentration for DDEAO and DDMAO at 25 °C

Thickening Function

The viscosities of DDEAO/AES and DDEAO/LAS complex solutions (the total active contents of the solutions were 20 wt%) were measured using a NDJ-79 rotating viscometer at room temperature.

Results and Discussion

Surface Activity

The critical micelle concentration (CMC) values and the surface tensions at CMC (γ_{CMC}) of DDEAO and DDMAO were determined from the plots of surface tension (γ) versus surfactant concentration as shown in Fig. 1. From the surface tension curves, the surface excess concentrations of DDEAO and DDMAO (Γ_{max}) were calculated from the Gibbs adsorption equation (1). The minimum surface area per surfactant molecule (A_{min}) was obtained from the Gibbs equation (2).

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

$$A_{min} = \frac{1}{N_A \Gamma_{max}} \quad (2)$$

where R is the gas constant, T is the absolute temperature, N_A is Avogadro's number and C is the concentration of surfactant in solution. For nonionic and zwitterionic surfactant, $n = 1$ [17–20]. The values of the surface excess concentration and the minimum surface area per surfactant molecule are presented in Table 1. As shown in Table 1, a slightly lower γ_{CMC} value for DDMAO than that of DDEAO was obtained, and the CMC value of DDEAO was

Table 1 Surface properties of DDEAO and DDMAO at 25 °C

Surfactant	CMC (mM)	γ_{CMC} (mN/m)	Γ_{max} (μmol/cm^2)	A_{min} (Å^2)	pC_{20}
DDMAO	0.75	23.9	4.97	33.4	4.17
DDEAO	0.38	25.4	5.20	31.9	4.39

obviously lower than that of DDMAO, which can be ascribed to the hydroxyethyl group of DDEAO giving a higher steric hindrance than the methyl of DDMAO and the better solubility of DDEAO. This result indicates that the surface activity of DDEAO is somewhat superior to that of DDMAO. For DDEAO, a higher value of Γ_{max} and a lower value of A_{min} than that of DDMAO, suggest a higher compactness of the aggregation. It is well established that the hydroxyethyl group of DDEAO is a dominant factor in the determination of Γ_{max} and A_{min} values.

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. The values of pC_{20} obtained for DDEAO and DDMAO are also presented in Table 1. From the values of pC_{20} in Table 1, the pC_{20} value of DDEAO is higher compared with that of DDMAO. This indicates that DDEAO is more easily adsorbed than DDMAO. This is probably due to the hydroxy group of DDEAO being able to form a hydrogen bond with water more easily.

Wetting Ability

Wetting ability is an important property for surfactants. The wetting abilities of DDEAO and DDMAO with different concentrations measured at room temperature are shown in Fig. 2. As shown in Fig. 2, the wetting ability of the surfactants improved with the increase in the concentration of the surfactants. That is because when surfactants wet the

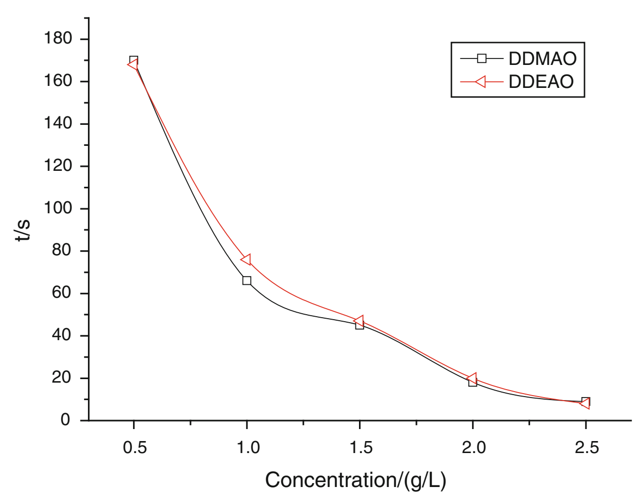

Fig. 2 The relation of different concentrations of DDEAO and DDMAO with wetting times

canvas disk, it will form a three-phase interface of ''solid–liquid–gas.'' Surfactants will adsorb to the interface of ''solid–liquid'' and that of ''liquid–gas;'' the more the surfactants adsorb onto the solid surface, the stronger is the wetting power on the canvas [15]. DDEAO and DDMAO show similar wetting ability. This is probably due to the fact that DDEAO and DDMAO have a similar γ_{CMC}.

Emulsifying Capacity

Emulsification is very important in many application processes, and it is therefore worth determining. The emulsifying capacity of the different concentrations of DDEAO 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 3 shows the results of the emulsifying capacity of DDEAO and DDMAO to emulsify soybean oil and liquid paraffin, respectively. The emulsifying capacity tends to increase with the increase in the concentration of DDEAO and DDMAO. The much longer time for soybean oil emulsion compared with that of liquid paraffin, suggests that DDEAO and DDMAO have a greater capacity to emulsify soybean oil than liquid paraffin. The capacity of DDMAO to emulsify soybean oil seems better than that of DDEAO, while DDEAO has a better emulsifying capacity for liquid paraffin.

Foaming Properties

Foaming is one of the important applications of surfactants. Foamability and foam stability are the two main measures of foam performances. The Ross-Miles method was used to test foaming properties of different times of different weight proportions of DDEAO/AES and DDEAO/LAS complex

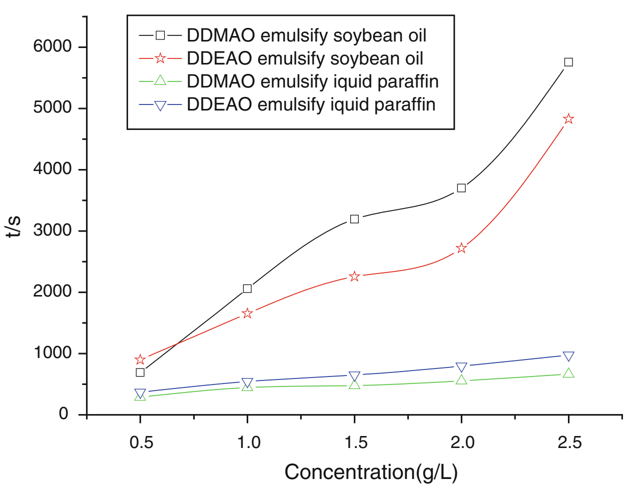

Fig. 3 The emulsifying capacity of DDEAO and DDMAO for soybean oil and liquid paraffin

Table 2 Foaming ability and foam stability of samples

Surfactant (weight proportion)	The volume of foam (ml)		$V_{10\ min}/V_{30\ s}$
	After 30 s	After 10 min	
DDEAO: AES			
0:1	340	285	0.84
1:5	390	365	0.94
1:10	405	375	0.92
1:15	440	415	0.94
1:20	445	410	0.92
1:0	550	495	0.90
DDEAO: LAS			
0:1	315	165	0.52
1:5	520	455	0.90
1:10	495	400	0.81
1:15	485	395	0.81
1:20	455	300	0.66

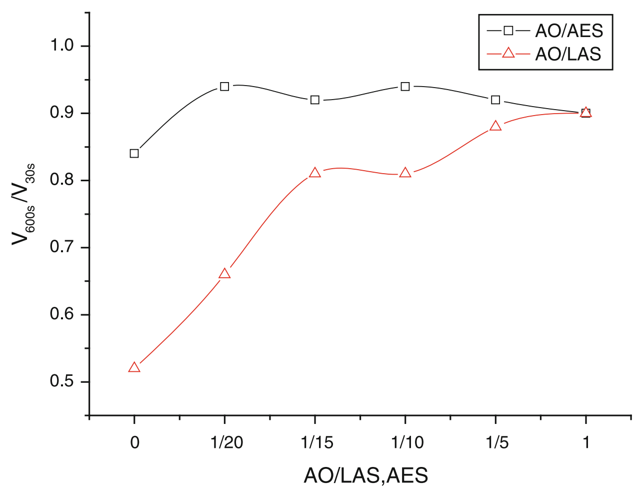

Fig. 4 The comparison of foam stability between DDEAO/AES and DDEAO/LAS mixture systems

systems with sample concentration of 2.5 g/l at 50 °C. The foaming ability is defined as the foam volume at 30 s and the foam stability is expressed by the ratio of the foam volumes after 10 min and 30 s. From the results presented in Table 2 and Fig. 4 two things may be said. First, DDEAO and the mixed surfactants have greater foaming abilities than that of single AES and LAS. Second, the foam stability of mixed surfactants is higher than that of single AES and LAS. For DDEAO/LAS complex systems, foam stabilities increase with increasing the DDEAO content. The results indicate that DDEAO is a superior foam stabilizer.

Thickening Function

Amine oxides generally exhibit a thickening effect and for this reason are usually added to shampoos. This effect of

Table 3 The viscosity of DDEAO/AES and DDEAO/LAS mixed surfactant systems

DDEAO (wt%)	The viscosity of DDEAO/AES mixed surfactants (mPa s)	The viscosity of DDEAO/LAS mixed surfactants (mPa s)
0	15	700
5	45	1,500
10	400	370
15	760	65
20	150	150

DDEAO was studied by a rotating viscometer. The viscosities of DDEAO/AES and DDEAO/LAS mixed surfactants, with a 20 wt% total active matter concentration, are shown in Table 3. Table 3 shows that for the DDEAO/AES mixed system, the viscosity achieved was the maximum when the content of DDEAO was 15 wt%, while it was at 5 wt% DDEAO for the DDEAO/LAS mixture.

Conclusions

Dodecyldiethoxylamine oxide (DDEAO) was synthesized, and its properties were compared with that of dodecyldimethylamine oxide (DDMAO). Surface activity measurements show that DDEAO has a slightly higher γ_{CMC} value and obviously a lower CMC than that of DDMAO. The two amine oxides have a similar wetting ability. Compared with DDMAO, the emulsifying capacity of DDEAO for liquid paraffin is superior. However, the emulsifying capacity of DDMAO for soybean oil is better than DDEAO. For AES and LAS, the foaming ability and foam stability are increased by adding DDEAO. The viscosity of DDEAO/AES and DDEAO/LAS mixed surfactants appears the maximum value at 15 wt% and 5 wt% DDEAO concentration, respectively. Consequently, DDEAO has potential applications as a foam stabilizer and thickening agent.

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References

1. Zhang H, Miller CA, Garrett PR, Raney KH (2005) Lauryl alcohol and amine oxides as foam stabilizers in the presence of hardness and oily soil. J Surf Deterg 8:99–107
2. Lim JC, Han DS (2011) Synthesis of dialkylamidoamine oxide surfactant and characterization of its dual function of detergency and softness. Colloids Surf A 389:166–174
3. Singh SK, Bajpai M, Tyagi VK (2006) Amine oxides: a review. J Oleo Sci 55:99–119
4. Mahajan RK, Sharma R (2011) Analysis of interfacial and micellar behavior of sodium dioctyl sulfosuccinate salt (AOT) with zwitterionic surfactants in aqueous media. J Colloid Interface Sci 363:275–283
5. Bakshi MS, Kaur G, Kaura A (2005) Effect of hydrophobicity of zwitterionic surfactants and triblock polymers on their mixed micelles: a fluorescence study. Colloids Surf A 269:72–79
6. Li F, Li G, Chen J (1998) Synergism in mixed zwitterionic-anionic surfactant solutions and the aggregation numbers of the mixed micelles. Colloids Surf A 145:167–174
7. Mclachlan A, Marangoni D (2006) Interactions between zwitterionic and conventional anionic and cationic surfactants. J Colloid Interface Sci 295:243–248
8. Garcia MT, Campos E, Ribosa I (2007) Biodegradability and ecotoxicity of amine oxide based surfactants. Chemosphere 69: 1574–1578
9. Kakehashi R, Yamamura S, Tokai N, Takeda T, Kaneda K, Yoshinaga K, Maeda H (2001) Hydrogen ion titration of long alkyl chain amine oxide micelles. J Colloid Interface Sci 243: 233–240
10. Bouguerra S, Letellier P, Turmine M (2010) Acid-base equilibrium of dodecyl dimethyl-amine-*N*-oxide micelles in water-butanol binary at 298 K. J Surf Deterg 13:217–224
11. Varade D, Joshi T, Aswal VK, Goyal PS, Hassan PA, Bahadur P (2005) Micellar behavior of mixtures of sodium dodecyl sulfate and dodecyldimethylamine oxide in aqueous solutions. Colloids Surf A 259:103–109
12. Abdel-Rahem RA (2012) Micellar parameters in solutions with cationic surfactants and *N*,*N*-dimethyldodecan-1-amine oxide: influence of cationic surfactant chain length. J Chem Eng Data 57:957–966
13. Li H, Wang X (2008) Single quantum dot-micelles coated with Gemini surfactant for selective recognition of a cation and an anion in aqueous solutions. Sens Actuators B Chem 134:238–244
14. Mao P (1988) Synthetic detergent industrial analysis. The publishing house of light industry, Peking, pp 456–462
15. Xu Q, Wang L, Xing F (2011) Synthesis and properties of dissymmetric gemini surfactants. J Surf Deterg 14:85–90
16. Wang GY, Du ZP, Zhang W, Cao QY (2009) Synthesis and surface properties of trisiloxane-modified oligo(ethylene oxide). Tenside Surf Deterg 46:214–217
17. Lu JR, Lee EM, Thomas RK (1993) Direct determination by neutron reflection of the structure of triethylene glycol monododecyl ether layers at the air/water interface. Langmuir 9: 1352–1360
18. Hines JD, Garrett PR, Rennie GK, Thomas RK, Penfold J (1997) Structure of an adsorbed layer of n-dodecyl-N, N-dimethylamino acetate at the air/solution interface as determined by neutron reflection. J Phys Chem B 101:7121–7126
19. Hines JD, Garrett PR, Rennie GK, Thomas RK, Penfold J (1997) Investigation of mixing in binary surfactant solutions by surface tension and neutron reflection: anionic/nonionic and zwitterionic/nonionic mixtures. J Phys Chem B 101:9215–9223
20. Eastoe J, Nave S, Downer A, Paul A, Rankin A, Tribe K (2000) Adsorption of ionic surfactants at the air-solution interface. Langmuir 16:4511–4518

Author Biographies

Ruitao Wang received a B.Sc. in chemical engineering and technology from Baoji University of Arts and Sciences, P. R. China in 2011 and is currently an M.Sc. student in applied chemistry at the China Research Institute of Daily Chemical Industry, P. R. China. He is involved in synthesis and applications of surfactants.

Yunling Li received a Ph.D. in applied chemistry from Shanxi University, P. R. China and is currently a professor of engineering at the China Research Institute of Daily Chemical Industry, P. R. China. Her research interests include surfactants and industrial catalysis.

Qiuxiao Li is currently a dean of China (RIDCI). He received his Ph.D. from the Chinese Academy of Sciences (2003). His research interests are focused on the engineering development related to manufactures of surfactants and their physical chemistry.