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Synthesis and Application Exploration of Novel Gemini Surfactant

XI-YUAN WU[1,2,*], HUI WANG[3] and GUI-RONG WANG[4]

[1]State Key Laboratory of Soil Erosion and Dryland Farming in the Loess Plateau, Institute of Water and Soil Conservation Chinese Academy of Sciences and Ministry of Water Resources, Northwest A&F University, Yangling 712100, Shaanxi Province, P.R. China
[2]Shandong Provincial Key Laboratory of Water and Soil Conservation and Environmental Protection, Linyi University, Linyi, Shandong, P.R. China
[3]Department of Chemical Engineering, University of Waterloo, 200 University Ave. West, Waterloo, Ontario, N2L 3G1, Canada
[4]Hangzhou Raw Seed Growing Farm, Hangzhou, P.R. China

*Corresponding author: Fax: +86 539 8766700; Tel: +86 15653975739; E-mail: wuxiyuan616@yahoo.com

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A novel gemini surfactant dichloride- *N,N,N′,N′*-tetramethyl- *N,N′*-dicetyl-2-propanol-1,3-ammonium (DTDPA) with two hydrocarbon chains connected by hydroxyl spacer chain was synthesized by three steps reactions. The values that characterized the solution properties of gemini surfactant including critical micelle concentrations (cmc), γcmc, pC20 and cmc/C20 were measured. The results demonstrated that the gemini surfactant gave low cmc, great efficiency in lowering the surface tension and strong adsorption at air/water interface. The application of DTDPA in the field of enhanced oil-recovery (EOR) technology and suspension copolymerization was investigated. DTDPA can reduce the interfacial tension of crude oil-water system sharply and maintain the viscosity of surfactant-PAM system excellently. The addition of DTDPA as assistant dispersant system can promote the oil absorption capacity of resin prepared by suspension copolymerization method within a range of concentration and reduce the oil absorption balanced time as increasing concentration of gemini surfactant.

Keywords: Gemini surfactant, EOR, Surfactant-polymer system, Suspension copolymerization, Resin, Oil absorption capacity.

INTRODUCTION

Since Bunton *et al.*[1] synthesized the cationic types of gemini surfactants, alkanediyl-α,ω-*bis*(alkyldimethylammonium) dibromide[1] and the gemini surfactant have been the most investigated surfactants.

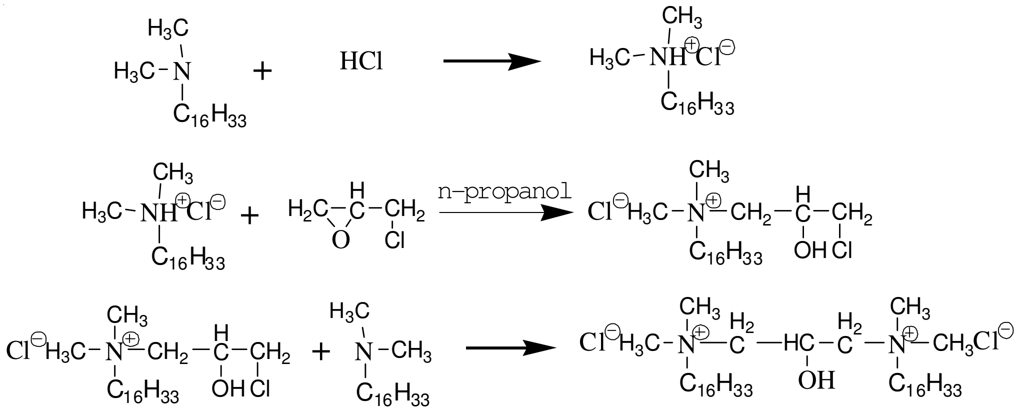
The gemini or dimeric surfactants with two hydrocarbon chains and two hydrophilic groups connected by spacer chain have been investigated actively[2-8]. The surfactants have superior properties compared with conventional monomeric surfactants, such as low critical micelle concentration (cmc) and C20 (surfactant concentration in the solution phase that can reduce the surface tension of the solvent by 20 mN m^{-1})[2-4]. In addition, the gemini surfactants are capable of increasing linear and branched thread-like micelles as well as closed ring micelles at extremely low concentrations. Gemini surfactants with short spacer groups even have unusual rheological properties[4,5], which bring gemini surfactants more research significances recently[6-8].

However, there were few reports concerning the application of gemini surfactants in the fields which were dominated by monomeric surfactants. It is important to promote the practical application as well as synthesis and physicochemical properties research of gemini surfactant, especially the quaternary ammonium gemini surfactants, which show more efficiency in reducing surface tension of water and interfacial tension at oil/water interface and stronger adsorption at solid/solution interface[9,10].

Enhanced oil-recovery (EOR) is a low-cost sources of new oil reserves and play a key role in maintaining steady oil production and long-term enhanced oil-recovery prospects remain good[11]. The alkali-surfactant-polymer (ASP) system is the most important techniques of enhanced oil-recovery realization. However, alkali existence cause increased amount of polymer, which need a large capital investment. Meanwhile, alkali can damage oil reservoir *via* scaling in underground wells. It is significant to figure out how to replace alkali-surfactant-polymer system using surfactant-polymer (SP) system or reduce the proportion of alkali in alkali-surfactant-polymer system.

In polymer chemistry field, the key step in suspension copolymerization process is to form and control the suspended particles. The addition of proper dispersant comprising surfactant will help to promote the performance of aimed polymer products.

We synthesized symmetric gemini quaternary ammonium salt cationic surfactant dichloride- *N,N,N′,N′*-tetramethyl- *N,N′*-dicetyl-2-propanol-1,3-ammonium (DTDPA) by three-step



Scheme-I: Synthesis reaction routes of Gemini surfactant DTDPA

reactions and investigated the potential application capability in the surfactant-polymer system of enhanced oil-recovery technology and preparation oil absorbency resin by suspension copolymerization as part of the dispersant system.

Scheme-I shows the reaction route for the synthesis of DTDPA used in this study.

EXPERIMENTAL

Dimethylcetylamine, epichlorohydrin (ECH), *n*-propanol, acetone, ethyl acetate, polyvinyl alcohol (PVA), benzoyl peroxide (BPO), ethyleneglycol dimethacrylate (EGDMA), lauryl acrylate (LA) and polyacrylamide (PAM) were purchased from Huadong Medicine Co., Ltd. (Hangzhou, China). They were used without further purification. All of the other chemicals used were of reagent grade. Triply distilled water was used in all of the measurements.

Synthesis of DTDPA: The dimethylcetylamine was added to the stirred mixture solution of distilled water and hydrochloric acid the speed of 5-7 drops per minute. The temperature was maintained at 45 °C using digital circulating water bath. The mixture was refluxed reaction for 3 h. The intermediate products were produced at 70 °C with added *n*-propanol to intermediates mixture. Then, ECH was added to mixture at the speed of 15-50 drops per minute. The mixture was refluxed for 1 h, the dimethylcetylamine was added to the reaction which was carried out for 6 h. The raw compound was washed using acetone and then recrystallized triply from mixtures of acetone and ethyl acetate. The aimed-compound as white solid was obtained after low temperature vacuum drying. The yield was 51.60 %. The structure was confirmed by FTIR (NICOLET 560 ESP). There were ν(O-H) in 3425.98 cm^{-1}, ν($-CH_3$) in 2918.09 cm^{-1}, ν($-CH_2-$) in 2850.11 cm^{-1}, δ(C-H) in 1467.93 cm^{-1} and no δ(C-N) in 1220-1020 cm^{-1}, which showed the dimethylcetylamine had reacted completely into DTDPA. The melting point was 73 °C, which was obtained by TG-DTA-DTG analyses (Beijing Optical Instrument Factory WCT-2). Equilibrium surface tension: the surface tension of aqueous solutions was measured with drop volume method. Sets of measurements to obtain equilibrium surface tension were taken until surface tension was changed less than 0.05 mN m^{-1} per 5 min. The cmc was obtained from the breakpoint of logarithm curve of surface tension *versus* concentration. Surface tension at cmc (γcmc) and C20 were also showed by the curve. The efficiency and effectiveness can be characterized by the negative value (pC20) of logarithm of surfactant concentration C20 and the value of cmc/C20 ratio[2], respectively. The pC20 measures the efficiency of surface adsorption and cmc/C20 ratio is a trending measure of surfactant to adsorb at the air/water interface related to its tendency to form micelles in the solution[2].

Suspension copolymerization: A type of polyacrylate high oil absorbency resin was prepared by suspension copolymerization technology. Polyvinyl alcohol and DTDPA composite system were as dispersant first time, ethyleneglycol dimethacrylate as crosslinking monomer, lauryl acrylate as monomer initiated by benzoyl peroxide, paraffine as fillers to promote the absorption performance. The optimized recipe was as follows: the ratio of DTDPA and PVA is 2:3, LA: EGDMA: BPO = 100:1:2. The whole experiment process was conducted under protection of nitrogen.

Methodologies of oil absorption experiments: The performance of oil sorbent is commonly rated by its absorption weight per unit weight (g/g)[12]. The procedure for determining oil absorption capacity generally followed the standard method defined by the American Society for Testing and Materials (ASTM)[13]. The oil absorbency was calculated according to the following equation:

$$\text{Oil Absorbency Capacity (W) (g/g)} = \frac{W_T - W_C - W_A}{W_A} \quad (1)$$

where W_T is the total weight (g) of the oil, test container and absorbent, W_C is the weight of test container (g) and W_A is the dry weight of absorbent (g)[14].

RESULTS AND DISCUSSION

Equilibrium surface tension: Table-1 shows the difference of equilibrium surface tension between gemini surfactant DTDPA and the conventional typical monomeric surfactants.

Table-1 lists the values of the cmc, surface tension at cmc (γcmc), pC20 and cmc/C20 along with the data of typical monomeric surfactant of sodium dodecyl benzene sulfonate (SDBS), the anionic monomeric surfactant sodium dodecyl sulfate (SDS) and the cationic monomeric surfactant trimethyl dodecyl ammonium bromide (TDAB).

As expected, DTDPA provides lower cmc and higher efficiency in lowering the surface tension than the monomeric surfactants. It is notable that the cmc of DTDPA is smaller by two or three orders of magnitude approximately than that of monomeric surfactants. This suggests the present gemini surfactants make it easy to form micelles in the bulk solution.

TABLE-1
COMPARISONS BETWEEN DTDPA AND TYPICAL MONOMERIC SURFACTANTS

Surfactants	cmc (mol L^{-1})	γcmc (mN m^{-1})	p*C*20	cmc/*C*20
DTDPA	8.00×10^{-4}	31.50	3.82	5.33
SDBS	1.20×10^{-3}	32.55	3.30	2.40
$C_{12}H_{25}SO_4Na$	8.00×10^{-3}	38.00	2.39	1.95
$C_{12}H_{25}N(CH_3)_3Br$	1.60×10^{-2}	40.00	-	-

The efficiency and effectiveness can be characterized by value of pC20 and cmc/C20, respectively. The pC20 value measures the efficiency of adsorption of surfactant at the air/water interface. Larger value of pC20 leads to greater tendency of surfactant to adsorb at air/water interface, related to its tendency to form micelles and it reduces the surface tension more efficiently. The value of cmc/C20 ratio is a convenient way to measure, which can be correlated with structural factors on the micellization and adsorption processes. Larger values of cmc/C20 ratio also lead to greater tendency of surfactant to adsorb at the interface, related to its tendency to form micelles[2].

The value of pC20 of DTDPA is larger than those of monomeric surfactants of SDBS, TDAB and SDS. It can be explained that longer hydrocarbon chains of the gemini surfactants lead to stronger adsorption at the air/water interface. The values of cmc/C20 of DTDPA are much high than those of monomeric surfactants. This indicates gemini surfactants adsorb at the air/water interface easier and larger cmc/C20 ratio probably reflects the difficulties of packing two hydrophobic groups in micelle.

Application research of DTDPA in the enhanced oil-recovery technology

Effect of DTDPA on equilibrium interfacial tension of crude oil-water system: Fig. 1 show the variation of the equilibrium interfacial tension (IFT) of crude oil-water system as the increase concentration of gemini surfactant DTDPA. In order to make the experiment results more close to the real gemini surfactant flooding application conditions, crude oil from Shengli Oil Field (East China) was used.

Fig.1 shows that the interfacial tension of oil-water system can be reduced sharply to ultra-low level (< 10^{-4} mN m^{-1}) with a wide range from 50 to 0.007 mN m^{-1} until the DTDPA concentration reaches 2 g L^{-1}. At 2 g L^{-1} of DTDPA concentration, there is a minimal value of interfacial tension of oil-water system as as 10^{-5}. The interfacial tension increases a bit as the increases of DTDPA with the concentration of DTDPA more than 2 g L^{-1}. It can be explained as follows: the ingredient of crude oil is more complex than the oil on sale and crude oil contains few interface activity materials, which can take synergistic effect with gemini surfactants in reducing interfacial tension of crude oil-water and at a certain surfactants concentration. It can keep the interfacial tension lower.

At present, surfactant flooding is very complex and has the highest degree of uncertainty. If the surfactant formulation for enhanced oil-recovery (EOR) is properly designed and the flow of the formulation is properly controlled in the oil reservoir, it has a high potential for achieving maximum oil recovery (MOR). As gemini surfactant has obvious advantages in reducing the equilibrium interfacial tension of oil-water

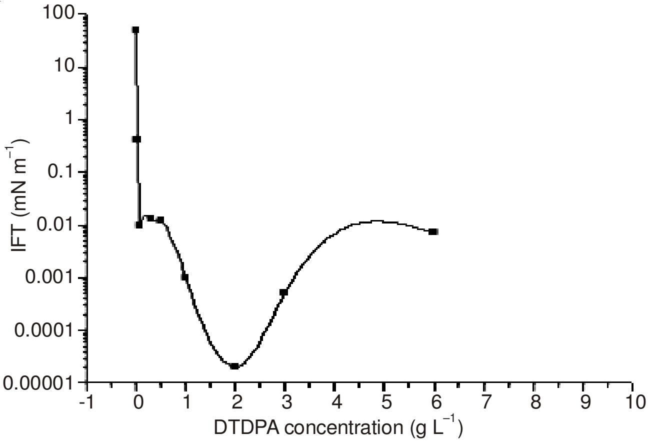


Fig. 1. Interfacial tension between crude oil and water at different concentration of DTDPA

system compared with the monomeric surfactant and also it has a high potential to be used in surfactant-polymer (SP) and even as a single component without other additives which would avoid chromatographic separation, which will be used in surfactant flooding more widely. Therefore, the research of gemini surfactants is very important and significant for both theories and practices.

Viscosity variation research of surfactant-polymer system: In order to investigate the feasibility of the surfactant-polymer system further to replace the alkali-surfactant-polymer system, it is necessary to study the viscosity variation of gemini surfactant and polymer binary system. The polyacrylamide (PAM) was chosen as the experimental polymer because PAM is the most widespread and efficient used polymer in polymer flooding field. The PAM solution with 1000 ppm was prepared and viscometer (Haake RV-20) was implemented to measure viscosity variation in 30 days of the binary system with different concentration of gemini surfactant (Fig. 2). Fig. 2 shows that the viscosity of binary system decreases with the increases of DTDPA concentration. The binary viscosity decreases with the days passed by. The viscosity loss of binary system in 30 days is demonstrated in Table-2. The values show that the gemini surfactant-polymer system is efficient in viscosity maintenance capability.

Application research of DTDPA in suspension copolymerization: The types, properties and amount of the dispersant are critical to determine the resin particle diameters and other characteristics and further to influence the performance of the

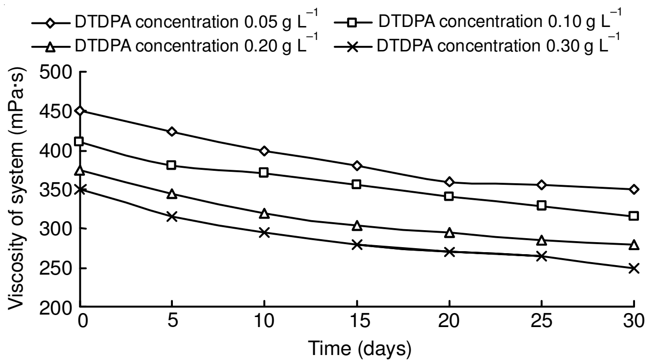


Fig. 2. Variation of viscosity of surfactant-polymer system with DTDPA concentration

TABLE-2
LOSS OF VISCOSITY OF
SURFACTANT-POLYMER SYSTEM (30D)

C_{DTDPA} (g L^{-1})	0.050	0.10	0.20	0.30
Loss percentage (%)	22.22	23.17	25.33	28.57

oil absorption resin. However, the single dispersant is not enough to satisfy the requirements to prepare the excellent performance absorbents. For example, the polyvinyl alcohol (PVA) is a commonly used dispersant, but PVA has lower capability to reduce the equilibrium surface tension. When the concentration of PVA is 0.1-0.2 wt. %, the surface tension of solvent reach 50-60 mN m^{-1}. Therefore, it is necessary to add surfactant to the reaction system to reduce surface tension. When DTDPA is added into the reaction system, it mainly plays roles in two aspects. DTDPA increases the adhesive effect of medium so that the particles have fewer chances to adhere each other. Meanwhile, resin's diameter can reach much smaller range as the reduction of surface tension.

Crude oil from Shengli oil field (East China) was used to be test oil. Fig. 3 shows the effects of different concentrations of gemini surfactant on the oil absorption capacities and rates of absorbents. It shows that the absorption oil balanced time of absorbent decreases with the increases of the concentration of DTDPA. There is no addition of DTDPA, so it need more than 100 min when concentration of DTDPA reaches 0.15 wt. %, it needs less than 50 min.

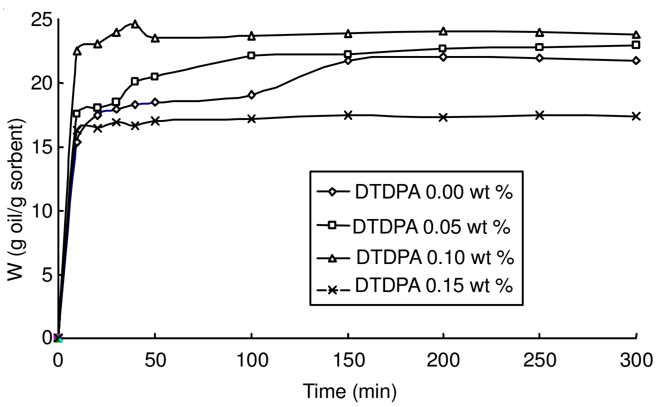


Fig. 3. Effect curve of DTDPA concentration on the oil absorption capacity of resin. EGDMA = 0.4 wt. %, BPO = 0.8 wt. %, PVA = 0.15 wt. %

Fig. 3 also indicates that there is a maximum oil absorption capacity with the variation of DTDPA concentration from 0 to 0.15 wt. %. It means an optimum DTDPA concentration in the preparation process of the high oil absorption resin.

Conclusions

• The cmc, γcmc, pC20 and cmc/C20 showed gemini surfactant has quite low cmc and can reduce surface tension efficiently. In addition, gemini surfactant was adsorbed at the air/water surface rather than form the micelles.

• The DTDPA-PAM system has better feasibility to replace alkali-surfactant-polymer system based on its excellent crude oil-water system interfacial tension reduction and viscosity maintenance.

• As one component of dispersant system in suspension copolymerization, DTDPA can assist the PVA to disperse the monomer particles evenly and promote resin performance characterized by oil absorption capacity and balanced time.

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