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The effect of anion on cationic surfactants and a structure-efficiency relationship study

Jie Zhang[a,*], Yun Bai[a], Weichao Du[a], Ya Wu[a], Xuefan Gu[a], Hong Li[a], Yun Ma[a,b], Chengtun Qu[a,b], Gang Chen[a,c,*]

[a]*College of Chemistry and Chemical Engineering, Xi'an Shiyou University, Xi'an, Shaanxi 710065, China, emails: zhangjie@xsyu.edu.cn (J. Zhang), gangchen@xsyu.edu.cn (G. Chen), 2453107878@qq.com (Y. Bai), duweichao@xsyu.edu.cn (W. Du), wuya@xsyu.edu.cn (Y. Wu), xuefangu@xsyu.edu.cn (X. Gu), 841911637@qq.com (H. Li), mayun9401@xsyu.edu.cn (Y. Ma), xianquct@xsyu.edu.cn (C. Qu)*

[b]*Shaanxi Province Key Laboratory of Environmental Pollution Control and Reservoir Protection Technology of Oilfields, Xi'an, 710065, China*

[c]*State Key Laboratory of Petroleum Pollution Control, CNPC Research Institute of Safety and Environmental Technology, Beijing 102206, China*

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ABSTRACT

To study the effect of non-surface activity anions on the ammonium, four quaternary ammonium cationic surfactants, cetyltrimethylammonium fluorine (CTAF), cetyltrimethylammonium chlorine (CTAC), cetyltrimethylammonium bromine (CTAB), and cetyltrimethylammonium iodine (CTAI), were evaluated by surface tension, foam ability, emulsification power, and corrosion inhibition. The results showed that the anion has a deep effect on cationic surfactants. The surface tension follows the order of CTAI < CTAB < CTAF < CTAC, the foaming ability follows the order of CTAC < CTAF < CTAB < CTAI, the emulsification ability follows the order of CTAF < CTAC < CTAB < CTAI, and the corrosion inhibition effect follows the order of CTAF < CTAC < CTAB < CTAI.

Keywords: Cationic surfactants; Surface tension; Foam; Emulsification; Corrosion inhibition; Structure-efficiency relationship

1. Introduction

Cationic surfactants have attracted the attention of chemists for a long time, due to their generally simple synthesis and their broad application in several fields [1]. They are important as ingredients of cosmetic products and are also used as corrosion inhibitors [2] in emulsion polymerization [3] and textile processing [4]. The most important class of cationic surfactants is quaternary ammonium salts. In previous study, countless papers have studied many kinds of quaternary ammonium cationic surfactants, and most of the researchers have managed to alter the number of carbon atoms to synthesis different quaternary ammonium cationic surfactants [5], while the corresponding anions are usually Cl^- and Br^-. Nevertheless, the effect of anion groups on the property of cationic surfactants has received a little attention. In this work, we used four quaternary ammonium cationic surfactants, cetyltrimethylammonium fluorine (CTAF), cetyltrimethylammonium chlorine (CTAC), cetyltrimethylammonium bromine (CTAB), and cetyltrimethylammonium iodine (CTAI), to study the effect of non-surface activity anions on the same ammonium, by evaluating the interfacial properties such as surface tension, foam ability, emulsification power, and corrosion inhibition.

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* Corresponding authors.

2. Experimental procedure

2.1. Materials

CTAF, CTAC, CTAB, and CTAI were purchased from China National Pharmaceutical Group (Beijing). Their structures are shown in Fig. 1. Other chemicals were purchased from Xi'an Chemical Reagent Factory (Xi'an China) and were used without further purification.

2.2. Surface tension measurement

Hanging ring method is one of frequently used methods to measure surface tension of different surfactants solution. The surface tension of the surfactants solution with a concentration range of 10–3,000 mg/L was measured by means of a Krüss-K 6 tensiometer (Krüss K 100, Germany) at 25°C [6]. The platinum ring was frequently washed by distilled water to obtain the standard surface tension value of the distilled water. All measured values of surface tension were repeated triple to reduce the error [7].

2.3. Foaming ability and stability measurement

There are many methods to generate foam, including the sparge tube technique, gas flow "whipping", and Ross–Miles method, in which Ross–Miles method was used as a standard method to evaluate the foam-discharging agent in gas field. In this study, the Ross–Miles method was used to evaluate the foam properties of surfactant solutions [8,9]. To avoid long-lasting measurements of decay of the foam height, the R_5 parameter is proposed as the quotient of the foam height after 5 min to the initial foam height. In this study, the initial foam height h_0 and residual foam height h_5 were measured for all surfactants. The residual foam ratio R_5 was calculated as the ratio of the 5-min foam height h_5 to the initial foam height h_0 as follows:

$$R_5 = (h_5/h_0) \times 100\% \quad (1)$$

2.4. Microstructure of foams

The microstructure of foam was characterized under a microscope using a polarizing microscope (DM4500P LFD, Germany).

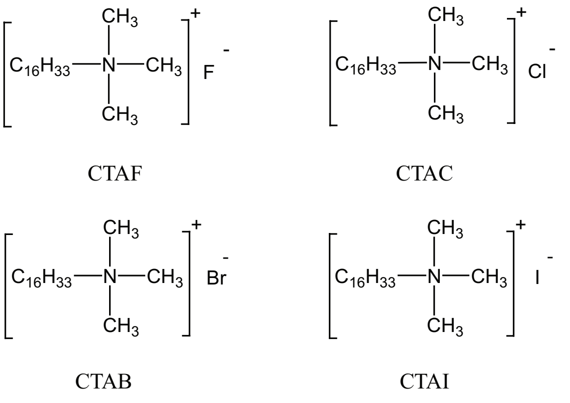

Fig. 1. Structures of the four surfactants.

2.5. Emulsification

To determine the emulsification power of different cationic surfactants solution, 10 mL surfactant solution and 10 mL crude oil were placed in a plug test tube of 20 mL capacity, which was placed in a regulated temperature instrument at 60°C [10]. Subsequently the tube was vibrated for 2 min and then settled standing [11]. The stabilization of the four emulsions was estimated by means of the time demanded for separating different volume of four surfactant solutions.

2.6. Corrosion inhibition measurement

A weight loss technique was adopted to evaluate the inhibition efficiency of the four surfactants solution with different concentration in HCl solution at 303 K for 3 h [12]. The experiments were performed with mild steel specimens of 40 mm × 13 mm × 2 mm; these specimens were polished smooth by 360#, 600#, and 1,200# sandpapers before the experiment, subsequently, polished specimens were cleaned with distilled water, and then washed with absolute ethanol; finally with acetone. They were dried by degreasing cold air and placed in a dryer. Before the experiment, the length, width, thickness, and whole diameter were measured with Vernier caliper. These specimens were immersed in 5% HCl solution with different surfactants solution at 303 K for 3 h [13].

3. Result and discussion

3.1 Surface Activity

The surface tension of the four surfactants solution at various concentrations is shown in Fig. 2. It is extremely obvious that the surface tension decreases with the increase of concentration under the low concentration, and then it becomes steady as the concentration increases to a certain value [14]. The minimum surface tension and the critical micelle concentration (CMC) of surfactants were summarized in Table 1. As indicated, the CMC varies from 81.4 to 138.4 mg/L. At the concentration of 1,000 mg/L, the surface tension of CTAI is 29.98 mN/m, whereas for CTAB and CTAF, they reach 30.85 and 32.26 mN/m, respectively. Nevertheless, the CTAC shows the highest surface tension of 37.39 mN/m. It makes

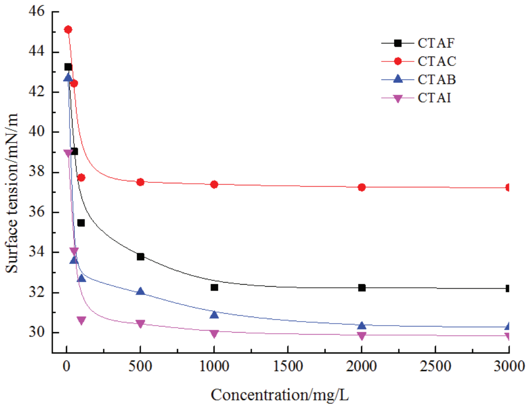

Fig. 2. Surface tension–concentration curves of different surfactants at same concentration.

clear that the capability of CTAI to decrease the surface tension is the most preeminent than that of other surfactants. This appearance fully reflects that the different anions can affect the surface activity [15,16].

3.2. Foaming ability

The stability of the foam was evaluated according to the initiative height of foam (h_0) and foam height after 5 min (H_5) after the mechanical agitation stopped at 25°C. The results are shown in Table 2. Foaming ability of the four surfactants is quite different, and the foaming height of same surfactant increases with increase of concentration and reaches to a maximum H_0 and H_5 at the concentration of around 2,000 mg/L. Beyond this concentration, H_0 and H_5 remain almost stable. So 2,000 mg/L is referred as the optimal concentration for different surfactants solution. The CTAI exhibits the optimal foaming ability, and H_0 reaches 22.5 mL, H_5 22.0 mL, and R_5 97.8%.

There are many factors affecting the foaming ability and stability, such as surface tension, structures and types of surfactants, electrostatic charges, and so on [17–19]. To compare the surface tension of difference surfactants, it can be found that the surface tension of CTAI is the lowest, and its foaming ability and stability is the highest. It unambiguously illustrates that surface tension is not the only decisive factor for foaming ability and stability. The four surfactants possess quite different anion groups even though their hydrophobic groups are the same. However, the anion group is I^-, CTAI exhibits excellent foaming ability and stability.

3.3. Microstructure of foams

Optical microscopy was used to characterize the microstructures of the foam produced by the four surfactants solution with an agitation speed 7,000 rpm for 3 min [20]. The result is shown in Fig. 3. It can be seen from the figures that foam produced from different surfactants solution present different shapes and volume. The foam of CTAF and CTAC exhibits spherical shape evidently, while the foam of CTAI is still irregular polygon, which illustrates non-surface active anions exert different influence on microstructure of the foam. This may be attributed to the fact that the foam stability is controlled by the liquid film drainage process. Compared with other surfactants, the drainage process of the CTAF is the slowest, so the foam produced by CTAF has a high stability.

Table 1
The CMC and surface tension of different surfactants under 1,000 mg/L

Surfactant	CMC, mg/L	The minimum surface tension, mN/m
CTAF	138.4	32.0
CTAC	98.9	37.0
CTAB	81.4	30.1
CTAI	109.9	29.8

3.4. Emulsification power

Emulsification power is also a significant aspect of surfactants solution in the presence of oil phase. The stabilization of the shaped emulsion between the surfactants solution and the oil phase depends on the chemical structure of cationic surfactant and the oil, moreover, the emulsification power is also related to the surface activity [21]. The stabilization of emulsions cling to different surfactant assimilation shaping a protected membrane at the membrane of the dispersed droplets which is likely to postpone or hinder combination. Cationic surfactants strengthen stabilization by means of rendering an electrostatic charge on the droplet surface accordingly reducing the contact

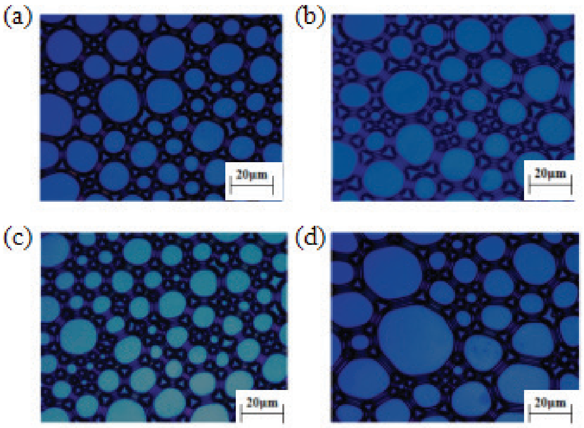

Fig. 3. Microscope morphology of different surfactant (a) CTAF, (b) CTAC, (c) CTAB, and (d) CTAI.

Table 2
The foaming performance of different concentration of different surfactant

Concentration, mg/L	The foaming ability and stability											
	CTAF			CTAC			CTAB			CTAI		
	h_0, mL	h_5, mL	R_5, %	h_0, mL	h_5, mL	R_5, %	h_0, mL	h_5, mL	R_5, %	h_0, mL	h_5, mL	R_5, %
40	12.8	9.8	76.6	12.5	7.2	57.6	13.5	8.8	65.2	14.5	11.5	79.3
60	15.2	11.8	77.6	14.2	9.8	69.0	15.9	12.5	78.6	16.5	14.0	84.8
100	16.9	14.2	84.0	16.8	11.7	69.6	17.5	15.2	86.9	18.2	17.0	93.4
200	19.7	18.5	93.9	18.2	14.8	81.3	20.3	19.5	96.1	21.5	20.5	95.3
300	20.5	19.8	96.6	18.3	16.2	88.5	21.8	21.0	96.3	22.5	22.0	97.8

between the droplets [22]. To a certain extent, the amount of surfactant adsorption at the oil–water interface in O/W emulsions depends on the degree to which the hydrophobic groups of the cationic surfactants damage the structure of the water phase [4]. Consequently, when the chain length retains constant, different anion is likely to affect the emulsion power. The data are listed in Fig. 4. It is extremely obvious that the half-life times of the four emulsions are less than 22 min. Compared with other surfactants, CTAI gets the highest emulsification ability, with the half-life time of 21.05 min. CTAB and CTAC lead to 16.62 and 13.33 min, respectively. CTAF shows the lowest emulsification ability, with the shortest half-life time of 10 min. Beyond doubt, the reason should be attribute to the effect of different anions on the distribution of cationic part. The mutual competition exists different surfactant molecules on the interface, resulting in disorder to the prearranged layers, which promotes the combination process [4]. The different surfactant molecules weight is likely to affect this process. The weight of CTAI molecule is the highest when compared with three surfactants, which can availably prevent combination [23]. It is clearly approved that different anions have a great significance on the ability of emulsification power.

3.5. Corrosion inhibition

Corrosion of steel alloys is the exceedingly critical issue emerging in virtue of the corrosive surroundings, which not only affects the original metal luster, but also brings about a great deal of economic expenses in a lot of technical fields. Accordingly, some inquirers have solved this issue as well as its prevention by means of usage of corrosion inhibitors. There are many types of corrosion inhibitors, including cationic, anionic, and nonionic surfactants, and so on [10]. The corrosion inhibition of the four surfactants was summarized in Table 3, where we could infer that different surfactants have inhibited the corrosion of the steel plates in 5% HCl solutions at all concentrations from 0.1 to 5.0 mg/L at 30°C. The values of inhibition efficiency (E_w%) and corrosion rate (W_{corr}) were summarized from the weight loss measurements with and without the addition of various concentrations of surfactants after 3 h of immersion in the 5% HCl solution at 30°C.

As seen, the inhibition efficiency increases with the increase in the concentration of different surfactants, which indicates that the number of molecules of inhibitors adsorbed over the steel samples surface increases. So the increased number of molecules prevents the active sites of acid from attacking to protect the steel surface from corrosion. From Table 3, the minimum efficiency was observed for CTAF (80.5%), followed by CTAC (87.60%), and CTAB (90.20%), yet the maximum was attained to CTAI (94.20%) at 5.0 mg/L of each additive, which could confirm that CTAI is more effective as inhibitors for the steel samples in 5% HCl solutions at the same temperature and concentration. It also shows that I^- effectively promotes the performance of corrosion inhibitors. As a result of the lower electronegativity and coordination ability of I^-, it helps to adsorb on the steel surface. From the angle of ion radius or electron cloud, the electron cloud of I^- is easier to deform and bond with iron, thus promoting the adsorption of CTAI on the surface of steel.

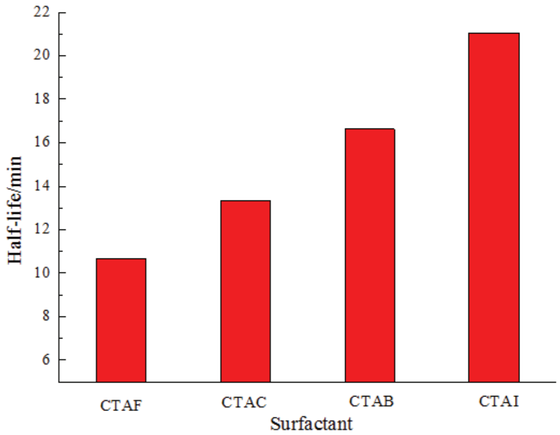

Fig. 4. The half-life of different cationic surfactants with same concentration.

Table 3
Corrosion rate and inhibitor efficiencies for various concentrations of inhibitor in 5% HCl at 30°C

Inhibitor	Concentrations, mg/L	W_{corr}, g/m·h	E_w, %
Blank	0	4.5142	–
CTAF	0.1	2.0314	55.00
	0.5	1.6748	62.90
	1.0	1.3633	69.80
	2.5	1.0879	75.90
	5.0	0.8803	80.50
CTAC	0.1	1.6793	62.80
	0.5	1.3994	69.00
	1.0	1.0925	75.80
	2.5	0.8035	82.20
	5.0	0.5598	87.60
CTAB	0.1	1.3588	69.90
	0.5	1.0925	75.80
	1.0	0.8025	82.50
	2.5	0.5643	87.50
	5.0	0.4424	90.20
CTAI	0.1	1.1286	75.00
	0.5	0.7765	82.80
	1.0	0.5648	87.50
	2.5	0.3250	92.80
	5.0	0.2618	94.20

4. Conclusions

In this work, we used four quaternary ammonium cationic surfactants to study the effect of different anions on the same ammonium. The results show that the anions affect the proprieties and abilities of the quaternary ammonium cationic surfactants obviously. The best results were obtained as following. The minimum surface tension is 29.8 mN/m at the concentration of 1,000 mg/L CTAI, and CTAI exhibits the optimal foaming ability, H_0 reached 22.5 mL and H_5 attained 22.0 mL. The corrosion inhibition efficiency in of CTAI solution reaches 94.2% in 5% HCl at 303 K. Compared with four surfactants, the optimal emulsification power is CTAI, and it takes 21.05 min.

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References

[1] P.E. Hellberg, Ortho ester-based cleavable cationic surfactants, J. Surfactants Deterg., 5 (2002) 217–227.

[2] O. Kirk, F.D. Pedersen, C.C. Fuglsang, Preparation and properties of a new type of carbohydrate-based cationic surfactant, J. Surfactants Deterg., 1 (1998) 32–41.

[3] T. Tatsumi, W. Zhang, T. Kida, Y. Nakatsuji, D. Ono, Novel hydrolysable and biodegradable cationic gemini surfactants: 1,3-bis[(acyloxyalkyl)-dimethylammonio]-2-hydroxypropane dichloride, J. Surfactants Deterg., 3 (2002) 167–168.

[4] D.Q. Xu, B.H. Qi, D. Fang, X.M. Zhang, T. Zhang, Preparation, characterization and properties of novel cationic gemini surfactants with rigid amido spacer groups, J. Surfactants Deterg., 19 (2016) 91–99.

[5] Y. Zhang, M.M. Ding, L.J. Zhou, H. Tan, J.H. Li, H.N. Xiao, J.S. Li, Synthesis and antibacterial characterization of gemini surfactant monomers and copolmers, Polym. Chem., 3 (2012) 907–910.

[6] A.M. Badawi, M.A. Hegazy, A.A. EL-Sawy, H.M. Ahmed, W.M. Kamel, Novel quaternary ammonium hydroxide cationic surfactants as corrosion inhibitor for carbon steel and as biocides for sulfate reducing bacteria (SRB), Mater. Chem. Phys., 124 (2010) 458–465.

[7] Y.J. Sheng, X.J. Wu, S.X. Lu, C.H. Li, Experimental study on foam properties of mixed systems of silicone and hydrocarbon surfactants, J. Surfactants Deterg., 19 (2016) 823–831.

[8] B.M. Folmer, B. Kronberg, Effect of surfactant polymer association on the stabilities of foams and thin films: sodium dodecyl sulfate and poly (vinyl pyrrolidone), Langmuir, 16 (2000) 5987–5992.

[9] K. Lunkenheimer, K. Malysa, Simple and generally applicable method of determination and evaluation of foam properties, J. Surfactants Deterg., 6 (2003) 69–74.

[10] N.A. Negm, A.F.M.E. Farargy, D.E. Mohammed, H.N. Mohamad, Environmentally friendly nonionic surfactants derived from tannic acid: synthesis, characterization and surface activity, J. Surfactants Deterg., 15 (2012) 433–443.

[11] A.M. Alsabagh, D.R.K. Harding, N.G. Kandile, A.M. Badawi, A.E. EI-Tabey, Synthesis of some novel nonionic ethoxylated surfactants based on α-amino acids and investigation of their surface active properties, J. Dispersion Sci. Technol., 30 (2009) 427–438.

[12] N.A. Nagm, I.A. Aiad, Synthesis and characterization of multifunctional surfactants in oil-field protection applications, J. Surfactants Deterg., 10 (2007) 87–92.

[13] N.A. Nagm, M.F. Zaki, M.A.I. Salem, Synthesis and evaluation of 4-diethyl amino benzaldehyde Schiff base cationic amphiphiles as corrosion inhibitors for carbon steel in different acidic media, J. Surfactants Deterg., 12 (2009) 321–329.

[14] N.A. Negm, A.A. Mohamed, M.Y. El-Awady, Influence of structure on the cationic polytriethanol ammonium bromide derivatives. I. Synthesis, surface and thermodynamic properties, Egypt. J. Chem., 47 (2004) 369–381.

[15] S. Sett, R.P. Sahu, D.D. Pelot, A.L. Yarin, Enhanced foamability of sodium dodecyl sulfate surfactant mixed with super-spreader trisiloxane-(poly)ethoxylate, Langmuir, 30 (2014) 14765–14775.

[16] A. Bera, K. Ojha, A. Mandal, Synergistic effect of mixed surfactant systems on foam behavior and surface tension, J. Surfactants Deterg., 16 (2013) 621–630.

[17] D.P. Acharya, J.M. Gutiérrez, K. Aramaki, K.I. Aratani, H. Kunieda, Interfacial properties and foam stability effect of novel gemini-type surfactants in aqueous solution, J. Colloid Interface Sci., 291 (2005) 236–243.

[18] E. Santini, F. Ravera, M. Ferrari, C. Stubenrauch, A. Makievski, J. Krägel, A surface rheological study of non-ionic surfactants at the water-air interface and the stability of the stability of the corresponding thin foam films, Colloids Surf., A, 298 (2007) 12–21.

[19] A. Pinazo, L. Pérez, M.R. Infante, E.I. Franses, Relation of foam stability to solution and surface properties of gemini cationic surfactants derived from arginine, Colloids Surf., A, 189 (2001) 225–235.

[20] A.M. Alsabagh, Surface activity and thermodynamic properties of water-soluble polyester surfactants based on 1,3-dicarboxymethoxybenzene used for enhanced oil recovery, Polym. Adv. Technol., 11 (2000) 48–56.

[21] N.S. Almed, A.M. Nassar, N.N. Zaki, H.K. Gharieb, Stability and rheology of heavy crude oil-in-water emulsion stabilized by an anionic-nonionic surfactant mixture, Pet. Sci. Techol., 17 (1991) 553–576.

[22] D.Q. Xu, B.H. Qi, D. Fang, X.M. Zhang, T. Zhang, Preparation, characterization and properties of novel cationic gemini surfactants with rigid amido spacer groups, J. Surfactants Deterg., 19 (2016) 91–99.

[23] G. Chen, D. Tao, An experimental study of stability of oil-water emulsion, Fuel Process. Technol., 86 (2005) 499–508.