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Surface Activity of Alcohol Ethoxylates of Natural Alcohol and Fischer-tropsch Oxo-Alcohol

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ABSTRACT

The differences between alcohol ethoxylates of natural alcohol and Fischer-tropsch oxo-alcohol were described in this paper. The alcohol ethoxylates were prepared by the one-step synthesis from Fischer-tropsch oxo-alcohols and linear alcohols. Equilibrium surface tension studies showed that the lowest surface tension of Fischer-tropsch oxo-alcohol ethoxylates was lower than for natural alcohol ethoxylates. The dynamic surface tension of Fischer-tropsch oxo-alcohol ethoxylates is better than the natural alcohol ethoxylates. Results show that in comparison with natural alcohols, Fischer-tropsch oxo alcohol ethoxylates have higher surface activity. Diversification of alcohol ethoxylates selection can help improve its physicochemical properties and enlarge its application fields.

Key words: Surface Activity, Alcohol Ethoxylates, Fischer-tropsch Oxo-Alcohol
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1. INTRODUCTION

Surfactants are used in daily and industrial applications, Alcohol ethoxylates which are produced from are made of an alkyl chain alcohol with *n* methylene groups and a hydrophilic part with *m* oxyethylene units [1-3]. Fatty alcohols currently are made of a variety of basic raw materials including natural fats and oils, natural gas, and petroleum [3]. Coal is one of the basic raw materials. Coal converted to Olefins via the Fischer-tropsch (F-T) process and then alcohols are formed in the conversion from Olefins via the oxo process.

Unlike natural alcohols, Fischer-tropsch oxo-alcohols is produced the hydroformylation of olefins obtained in the Fischer-tropsch (FT) process. It is the mixture of approximately 50% branched and 50% linear. Because the majority of the branching is not in the C-2 position, when it is further derivatized, it reacts more like a linear alcohol [2, 4].

However, fewer studies have focused on Fischer-tropsch oxo-alcohols ethoxylate performance. A greater diversification in the alcohol ethoxylates that are available will lead to a greater variety of physicochemical properties and expand the number of fields in which they can be used.

This paper describes the characteristics properties of Fischer-tropsch oxo alcohol ethoxylates (E2307 and E2310 in fig 1) in comparison with another conventional natural alcohol ethoxylate (AEO-9). Their equilibrium and dynamic surface tension at the air/aqueous solution interface were investigated. The purpose of this paper of the physicochemical properties of these alcohol ethoxylates of natural alcohol and Fischer-tropsch oxo-alcohol was to study their differences. Results show that in comparison with natural alcohols, Fischer-tropsch oxo alcohol ethoxylates have higher surface activity.
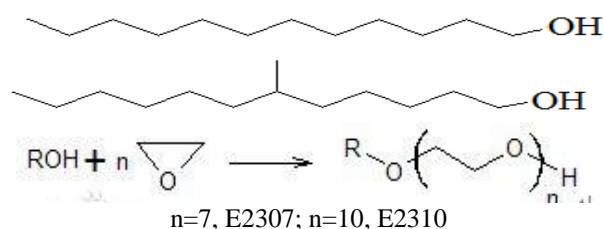

n=7, E2307; n=10, E2310
Fig. 1 the Fischer-tropsch oxo-alcohols ethoxylates

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2. EXPERIMENTAL METHODS

Materials

Fischer-tropsch oxo-alcohols ethoxylate (E2307 and E2310) was obtained from Sasol Chemical Co. All other chemicals were purchased from Sinopharm Chemical Reagent Co. All reagents were of analytical grades and were used as received. Double distilled water was used for all analysis and measurements of primary properties.

Equilibrium surface tension measurement

Concentrated stock solutions of surfactants were freshly prepared with doubly distilled water and then diluted to appropriate concentrations. Surface tension was measured by a KRUSS K100 Processor Tensiometer using the Wilhelmy plate method at 25.0 ± 0.1 °C [5-6]. The Wilhelmy platinum plate was 19.9 m in length and 0.2 mm in thickness. The dipping distance was 2 mm. The instrument was checked by doubly distilled water before each use. The platinum plate and the glassware were cleaned with strong basic solutions and rinsed with doubly distilled water. For every concentration, the surface tension was recorded three times with an average deviation of less than 0.2 mN·m^{-1}.

Dynamic surface tension

The dynamic surface tensions were measured using a Krüss bubble pressure tensiometer, model BP100. The dynamic surface tensions were measured in a time range between 10 ms and 200 s. The diameter of the capillary used in the bubble pressure measurements was about 0.2 mm. The sample cells were thermostated to 25.0 ±0.1 °C.

3. RESULTS AND DISCUSSIONS

Surface activity

The Surfactant can lower the surface tension of the medium in which it is dissolved, and the interfacial tension with other phases. The surface tension of liquid results from an imbalance of intermolecular attractive forces, the cohesive forces between molecules. The equilibrium surface tensions of dilute aqueous solutions of Fischer-tropsch oxo-alcohols ethoxylate (E2307 and E2310) and natural alcohol ethoxylate (AEO-9) were investigated shown in Figure 2. Obviously, the surface tension of three surfactants aqueous solution was reduced with increasing the surfactant concentration and then keeps almost constant, indicating that the molecules at air-liquid had reached the maximum adsorption equilibrium [5]. The critical micelle concentration (CMC) is determined from the break point in the curve. As shown in Figure 2, Fischer-tropsch Oxo-Alcohols ethoxylate is highly effective aqueous surfactant reducing the surface tension of water to 27-28 mN·m^{-1}. The values of γ_{cmc} are slightly lower than those (29.7 mN·m^{-1}) for natural alcohol ethoxylate and are similar to those reported for other branched surfactants [5]. The reason may be attributed to the fact that Fischer-tropsch oxo-alcohols are the mixture of branched chain (50%) and linear chain (50%), and the branched-chained AEO can provide the tight pack at the interface.
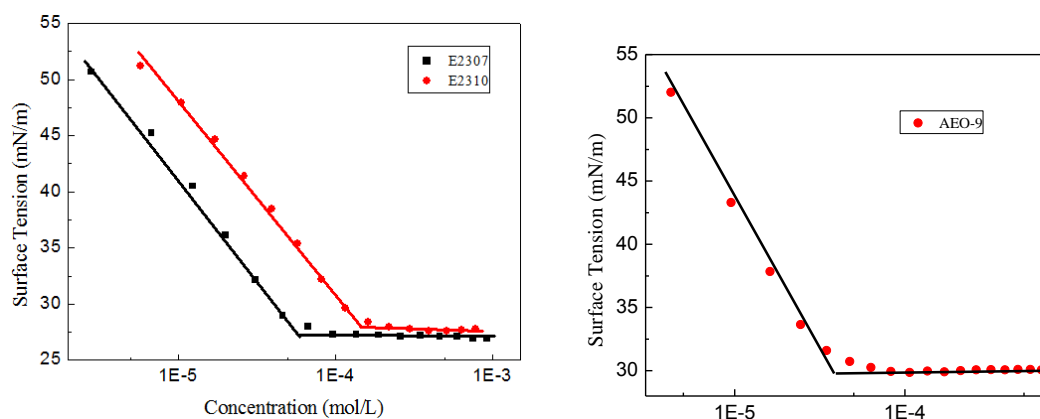

Fig. 2 The equilibrium surface tensions of the Fischer-tropsch oxo-alcohols ethoxylates and natural alcohol ethoxylate versus logarithm of molar concentration

By applying the approximate form of the Gibbs adsorption isotherm equations (eq 1 and 2) to the steeply descending, linear portion of the surface tension versus log concentration plots (Figure 2), the saturation adsorption values, Γ_{max}, at the air/water interface and the minimum area per surfactant molecule, A_m^s, at the air/water interface were calculated for each of the novel surfactants [7]. The adsorption data and A_m^s are as well as some hydrocarbon surfactants summarized in Table 1.

$$\Gamma_{max} = -\frac{1}{2.303RT}\left(\frac{\partial \gamma}{\partial \log c}\right)_T \tag{1}$$

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$$A_m^s = \frac{10^{16}}{N_A \Gamma_{\max}} \qquad (2)$$

$$\Delta G_{mic}^0 = RT \ln\left(\frac{cmc}{55.5}\right) \qquad (3)$$

$$\Delta G_{ads}^0 = RT \ln\left(\frac{C_\pi}{55.5}\right) - 6.022 \prod A_m^s \qquad (4)$$

Where $R = 8.3144$ J·mol^{-1}·K^{-1}, N_A is Avogadro's number, and A_m^s in Å^2 per molecule. Π (= γ_0-γ) the surface pressure in the region of surface saturation, and C_π the molar concentration of surfactant in the aqueous phase at a surface pressure Π (in mN·m^{-1}).

Table -1 Heterogeneous alcohol ethoxylates surfactants parameters at 25 ^{o}C

Surfactant	CMC (mol/L)	γ_{CMC} (mN/m)	Γmax (mol/cm^2)	A$_{cmc}$ (A^2/molecue)	ΔG_{mic}^0 (KJ/mol)	ΔG_{ads}^0 (KJ/mol)
E2307	5.70E-5	27.1	3.18 E-10	52.19	-34.1	-48.3
E2310	1.51E-4	28.0	2.79 E-10	59.64	-31.8	-47.6
AEO-9	4.0E-5	29.7	4.24E-10	39.20	-34.5	-44.5

The value for the standard free energy of micellization and adsorption is negative, showing tendencies to form micelles in solution and to adsorb at the air/water interface. Furthermore, ΔG_{ads}^0 is more negative than the corresponding ΔG_{mic}^0, indicating that the adsorption is the primary event as oppose to aggregation; this are comparable to reports in literature for other surfactants. The value of A_m^s for Fischer-tropsch oxo-alcohols ethoxylate is bigger than that of natural alcohol ethoxylate, Because the branched chains occupy more space than the linear chain.

Dynamic surface tensions

Lower equilibrium surface tensions for Surfactants are very significant; furthermore, the speed at which the surface tension is reduced is equally necessary [3]. Dynamic surface tension measurements were performed to investigate the kinetics of adsorption for three surfactants by the maximum bubble-pressure technique. Dynamic surface tension measurements were carried out at 1000 mg/L. The changes of the dynamic surface tension as a function of the surface age for surfactants is demonstrated in Figure 3. under the invested time range, relatively small variations in concentration result in massive change in surface tension. The surface tension is equal to that of water in shorter time. Furthermore, the shorter the time required attaining surface tension equilibrium is, the higher surfactant concentration; the equilibration is easier above the cmc than below it.
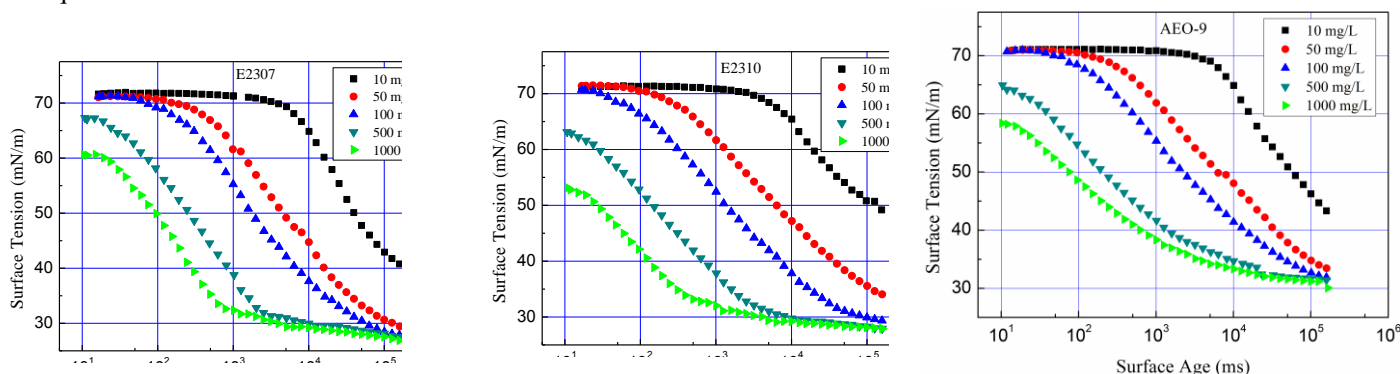

Fig. 3 Dynamic surface tension for E2307, E2307 and AEO-9 surfactant at 25 ^{o}C

Rosen Model can analyze the curves of the change in surface tension with time [1]. Rosen divided the dynamic surface tension into four region (Figure 4): an induction region (I), a rapid fall region (II), a mesoequilibrium region (III), and equilibrium (IV). Equation 5 can fit the three dynamic regions (I–III) of this plot:

$$(\gamma_0 - \gamma_t) / (\gamma_t - \gamma_m) = (t / t^*)^n \qquad (5)$$

Here γ_t is the surface tension of the surfactant solution at time t, γ_m is the meso-equilibrium surface tension (where γ_t has only a small change with time), and γ_0 is the surface tension of the pure solvent. Equation (5) can be changed into its logarithmic form to calculate the values of n and t*.

$$\log[(\gamma_0 - \gamma_t) / (\gamma_t - \gamma_m)] = n(\log t - \log t*) \qquad (6)$$

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The t* is the time required for γ_t to reach half of the value between γ_0 and γ_m, which is related to the surfactant concentration. n is a constant related to the molecular structure of the surfactant. It has been suggested that n is related to the difference between the energies of adsorption and desorption of the surfactant. The induction region ends when $(\gamma_0-\gamma_t)/(\gamma_t-\gamma_m) = 0.1$ and the rapid fall region ends when $(\gamma_0-\gamma_t)/(\gamma_t-\gamma_m) = 10$, then the meso-equilibrium region begins. To obtain the values of t_m and t_i, Equation (6) can be induced to the following equations

$$\log t_m = \log t^* + 1/n \tag{7}$$

$$\log t_i = \log t^* - 1/n \tag{8}$$

$$R_{1/2} = (\gamma_0 - \gamma_m)/2t^* \tag{9}$$

The value of t_m is time for the meso-equilibrium period to start; the value of t_i is time for the induction period to end. $R_{1/2}$ is the velocity to reduce surface tension by half of the difference between γ_0 and γ_m. The parameters coming from fitting equation 6 to the experimental data are described in table 2. The induction time t_i for E2307 is 0.0061 ms, which is shorter than that for AEO-9. Furthermore, the n values of surfactants have the connection with the diffusion energy while the t* values show the adsorption energy. A surfactant with lower t* value adsorbs to the interface more easily. Due to possessing lowest t*, E2310 reaches meso-equilibrium region the fastest, absorbs to the interface the easiest and has the lowest adsorption energy. $R_{1/2}$ values are velocity to reduce surface tension, the value of $R_{1/2}$ is E2310 > E2307 which is aligned with the trend of n values and a surfactant having larger surface excess value obviously needs more time to reach meso-equilibrium region.
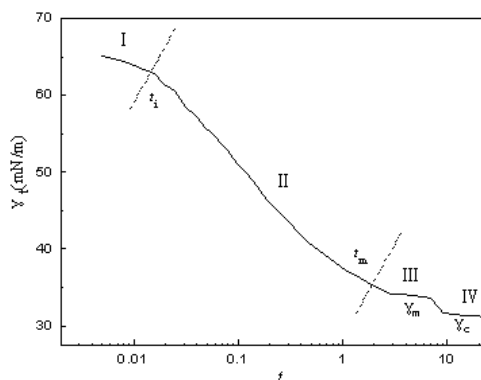

Fig. 4 The curves of the surface tension vs. time (Rosen)

Table -2 The DST parameters of surfactants with different concentrations at 25 ^{o}C

Surfactant	c mg/L	γ_m mN/m	n	t* s	t_m s	t_i s	$R_{1/2}$ mN·m^{-1}·s^{-1}
E2307	1000	31.5	0.951	0.068	0.770	0.0061	296.1
E2310	1000	32.6	1.028	0.027	0.250	0.0028	740.2
AEO-9	1000	32.6	0.616	0.052	2.184	0.1200	395.1

Obviously, the Fischer-tropsch oxo-alcohols ethoxylates have good dynamic surface tension. The reason is that Fischer-tropsch oxo-alcohol is approximately 50% branched and 50% linear. In generally, the branched surfactants have good dynamic surface tension than linear surfactants [8].

4. CONCLUSION

The Fischer-tropsch oxo-alcohols ethoxylates have good equilibrium and dynamic surface tension properties. They can reduce the surface tension of water to 27-28 mN·m^{-1} which are slightly lower than those (29.7 mN·m^{-1}) for natural alcohol ethoxylate. Furthermore, they can reduce the lowest surface tension at the shorter time. Fischer-tropsch oxo-alcohols ethoxylates are coal-based surfactants, which have more important applications in the future.

Notes
The authors declare no competing financial interest.

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