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ORIGINAL CONTRIBUTION

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Rheological properties of the aqueous mixtures of cationic-anionic surfactants

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Abstract The rheological properties of the aqueous mixtures of cationic-anionic surfactants, both in single-phase systems and in aqueous two-phase systems, have been studied. Bizarre rheological properties – negative thixotropy, viscoelasticity and high viscosity of shear rate dependent at relatively low concentration – have been observed. An unusual viscosity change, that is, viscosity lowering with increasing concentration, was obtained. The negative thixotropy might be due to the existence of lamellar or sheet-like micelles, viscoelasticity might be induced by rodlike and lamellar or sheet-like micelles, the high viscosity might be a consequence of the formation of network by long rodlike micelles and the concentration-induced viscosity lowering could be interpreted in terms of the decrease of micellar dimensions with concentration.

Key words Rheological property – cationic-anionic surfactants – negative thixotropy – viscoelasticity

Introduction

Considerable works have been done on the aqueous mixtures of cationic-anionic surfactants [1–10]. Most of the research activities have been focused on the surface adsorption and micellization phenomenon [1–5] as well as micellar dimensions and structures [6–9]. There were very few works dealing with their rheological properties [10] because such mixtures are often unstable – precipitation or phase separation usually occurs at very low concentrations (usually slightly beyond the CMC's) [5], making the study of rheological properties difficult.

Our studies have shown that, with the further increase of concentration, the mixtures form transparent homogeneous solutions at a higher concentration, this concentration range was called "high concentration region" (correspondingly, the concentration range in which precipitation or phase separation occurs was called "mediate concentration region") [11–12]. It was found that, in the high concentration region, especially in the boundary between the high concentration region and the mediate concentration region, the aqueous mixtures exhibit complicated rheological properties. So far as the systems we have studied are concerned, three kinds of bizarre rheological behaviors have been observed: negative thixotropy, viscoelasticity, and shear rate dependent high viscosity at relatively low concentration. Furthermore, an unusual viscosity change, that is, viscosity lowering with increasing concentration, has been obtained.

The negative thixotropy has been reported by us as a short communication [10]. In this paper, the full details of negative thixotropy and the other above-mentioned rheological properties of mixed cationic-anionic surfactants, both in single-phase systems and in aqueous two-phase systems have been studied.

Experimental

Materials

Sodium dodecylsulfate ($C_{12}S$) : Fluka Co. (Swiss), recrystallized from water-ethanol. Dodecyltriethylammonium bromide ($C_{12}NE$): prepared by mixing dodecane bromide with excess of triethylamine for 48 hours. The crude product of $C_{12}NE$ was recrystallized from acetone-ether. No surface tension minima were found for $C_{12}S$ and $C_{12}NE$, which implies that no surface active impurities exist in them. All water used was twice redistilled from alkaline permanganate.

Methods

Viscosity was measured by the reduced-pressure capillary viscometer which was set up in our laboratory [11]. Figure 1 is the sketch of the reduced-pressure capillary viscometer. At a reduced pressure, the flowing time (t) of a fixed amount of liquid through the capillary (from b to a) was measured. The apparent viscosity (η) was calculated by the following equation:

$$\eta = APt - B\rho_i/t$$
$$= A\,(\rho_e h_e - \rho_i h_i)\,t - B\rho_i/t$$

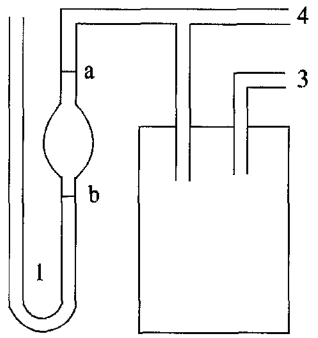
where P is the driving pressure making liquid flow through capillary, h_e is the height of liquid in manometer, h_i is the apparent height of measured liquid (h_i is varying during measurement, but the variation is the same when the volume of measured liquid is identical each time, so it is a constant), ρ_i and ρ_e are the densities of the measured liquid and the liquid in manometer respectively, A and B are all constants. The flow types could be judged by the relations between the driving pressure (P) and the apparent viscosity (η).

Viscoelasticity can be detected easily on the recoil of trapped bubbles which can be observed when such a solution is rotatively sheared and the shearing is stopped abruptly.

The negative thixotropy was judged using the reduced-pressure capillary viscometer and the concentric cylinder viscometer (Haake, Rotovisco).

After a solution was allowed to stand enough time, its viscosity (η_0) was measured using the reduced-pressure capillary viscometer. Soon after that, several measurements were carried out in quick succession, from which the largest value of viscosity (η_t) was taken. At last the solution was allowed to stand enough time again and its viscosity (η_0') was measured. All measurements were carried out at the same driving pressure. If $\eta_t > \eta_0$ and $\eta_0 = \eta_0'$, the solution should be negative thixotropic.

Fig. 1 Reduced-pressure capillary viscometer 1. Ostwald capillary viscometer, 2. Gas box, 3. To water pump, 4. To U manometer



When the concentric cylinder viscometer was used, the change of viscosity with time was measured at constant shear rate.

Results and Discussions

Negative thixotropy

Negative thixotropy is a rheological phenomenon defined as a reversible increase in viscosity with time when a liquid flows at constant shear rate. This phenomenon was found in some polymers [13], very few dispersing systems [14] and oil-water microemulsion [15]. To surfactant solutions, negative thixotropy is seldom seen [16–18]. In the course of our investigation of mixed surfactants, negative thixotropy was observed in the aqueous mixtures of cationic-anionic surfactants. Figure 2 shows the region

Fig. 2 Regions of negative thixotropy and viscoelasticity of $C_{12}NE$-$C_{12}S$(25 °C) —— negative thixotropy ----- viscoelasticity

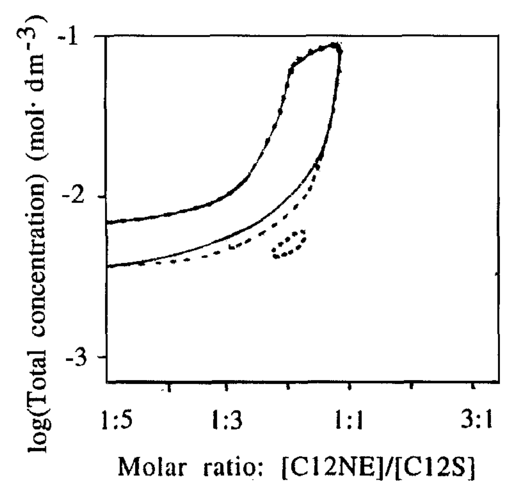


Table 1 Negative thixotropy of C_{12} NE-C_{12} S system (25 °C)

System	P (cm H_2O)	η_0 (cp)	η_t (cp)	η_0' (cp)
c_{12}NE-C_{12}S 0.01 mol · dm^{-3}* 1:2**	17.7	1.09	2.32	1.10
C_{12}NE-C_{12}S 8.0×10^{-3} mol · dm^{-3} 1:2	10.1	1.36	3.52	1.38

* Total concentration
** Molar ratio ([C_{12}NE]/[C_{12}S])

Table 2 Negative thixotropy of C_{12} NE-C_{12} S system (21 °C)

System	U	$S_{\min}$	$S_{\max}$	$t(s)$
c_{12}NE-C_{12}S 0.05 mol · dm^{-3} 1:2	18	5.4	10	225
C_{12}NE-C_{12}S 0.05 mol · dm^{-3} 1:1.5	27	2.8	4	50

where the mixtures of C_{12}NE and C_{12}S exhibit negative thixotropy.

Negative thixotropy could be judged easily by observing visually the increase of viscosity of solutions while the solutions were shaken. For example, 0.05 mol·dm^{-3}, 1: 2 C_{12}NE-C_{12}S solution is clear transparent on standing. It would be more and more viscous and become gel-like at last when it was shaken continuously. This gel-like fluid would restore gradually to the original state if it was allowed to stand enough time.

Tables 1–2 show the negative thixotropy of several typical solutions which were judged using the reduced-pressure capillary viscometer and the concentric cylinder viscometer (Haake, Rotovisco) respectively. In Table 2, U is the shear rate factor which corresponds to shear rate, S is the shear stress factor which corresponds to shear stress, $S_{\min}$ and $S_{\max}$ correspond to minimum and maximum shear stress respectively, t is the time between the onset of flow and the maximum of shear stress.

The negative thixotropic solutions have the following features:

(1) For the mixture of C_{12}NE and C_{12}S, negative thixotropy was observed only in nonequimolar systems with C_{12}S in excess.

(2) Negative thixotropic systems stand in the region between the high and the mediate concentration regions. The concentration forming negative thixotropic systems decreases with the increase of the amount of C_{12}S.

(3) Negative thixotropic solutions could be transparent homogenous, or opalescent or turbid. The transparency of solution varies with total concentration and molar ratio. The more close to 1: 1 the molar ratio is, or the lower the concentration is, the more poor the transparency of solution is. For example, 0.05 mol·dm^{-3}, 1: 2 C_{12}NE-C_{12}S solution is transparent homogenous, 0.05 mol·dm^{-3}, 1: 1.5, and 8.0 x 10^{-3} mol · dm^{-3}, 1: 2 C_{12}NE-C_{12}S solutions are opalescent. These opalescent or turbid solutions are usually quite stable, no obvious change of their appearances could be observed on standing for a long time.

(4) The negative thixotropic solutions are usually viscoelastic.

Up to now, there has been no theory of general agreement to explain the negative thixotropy of different systems. To the polymer and dispersing systems, four mechanisms have been proposed [13–14]: (1) aggregation theory, (2) crystallization theory, (3) network theory, (4) screen effect. For oil–water microemulsion systems, negative thixotropy was interpreted in terms of the existence of lamellar structures [15]. The shear thickening phenomenon of some micellar solutions was interpreted in terms of shear induced coagulation among rodlike micellar [16] and shear induced supermolecular structure [17].

For the mixtures of cationic-anionic surfactants, we thought that the negative thixotropy might be due to the existence of lamellar or sheet-like micelles.

The lamellar or sheet-like micelles are composed of parallel bilayers in which the water-layers are sandwiched. When the solution flows, it might be the sliding of bilayers in lamellar or sheet-like micelles with each other that leads to low viscosity of the solution. With the increase of shearing time, the parallel arrangement of bilayers would be gradually destroyed and become disordered, and consequently, viscosity increases with time. When the flow stops, the bilayers would return to the parallel arrangement gradually, which leads to the decrease of viscosity with time.

This possible mechanism may be evidenced by the fact that lamellar liquid crystal could be observed by polarizing microscope in some negative thixotropic solutions which were on standing for a long time, such as 0.04 mol · dm^{-3}, 1:1.5 C_{12}NE-C_{12}S. The lamellar liquid crystal could be regarded as a result of the growth of lamellar or sheet-like micelles.

Since the large size of the polar group of C_{12}NE is unfavorable to the parallel arrangement of surfactant molecules the mixtures of C_{12}NE and C_{12}S are not easy to form lamellar micelles when C_{12}NE is in excess. This might be the reason that negative thixotropy was observed only when C_{12}S is in excess.

For nonequimolar mixtures of cationic-anionic surfactants, the charge density on micellar surface increases with the increase of surfactant concentration and the amount of excess of component [7]. It is obvious that too low a charge density might be liable to induce precipitation or turbidity because of the coacervation or flocculation between micelles, and that too high a charge density might be liable to induce the formation of small micelles. On this ground, we might demonstrate the fact that negative thixotropy was observed on the boundary between the high and the mediate concentration regions, and the concentration forming negative thixotropic systems decreases with the increase of the amount of $C_{12}S$.

Viscoelasticity

Some aqueous surfactant solutions are viscoelastic, especially the surfactant systems with associating counter ions [19–21]. A typical set of systems is that of some cationic surfactants associating with certain aromatic organic compounds, such as alkyltrimethylammonium and alkylpyridinium salicylates with alkyl chain lengths from C_{12} to C_{16} [19–21].

For the aqueous mixtures of cationic-anionic surfactants, viscoelasticity could be observed at larger concentration range. Figure 2 shows the region in which the mixtures of $C_{12}NE$ and $C_{12}S$ exhibit viscoelasticity.

It could be observed that viscoelastic solutions have the following features:

(1) The same as the negative thixotropic solutions, viscoelasticity was observed in the region between the mediate and the high concentration regions.

(2) For the mixtures of $C_{12}NE$ and $C_{12}S$, viscoelasticity was observed only in nonequimolar systems with $C_{12}S$ in excess.

(3) Some viscoelastic solutions are negative thixotropic, which could be seen in Fig. 2.

(4) The viscoelastic solutions with negative thixotropy are usually quite stable, especially those which are clear transparent. Those without negative thixotropy are usually unstable, phase separation occurs and viscoelasticity vanishes on standing.

It used to be thought that the elastic properties were a consequence of the rodlike aggregates [19–21]. However, considerable investigations show that many systems also form rodlike aggregate but the solutions behave as normal Newtonian fluids even though the conditions are the same for which viscoelasticity had been observed previously. Hoffmann et al. thought that [22] it is because the chemical relaxation time for the formation of micelles is short (it is in the range of tenths of seconds) and no permanent network can be formed.

In our studies on the aqueous mixtures of cationic-anionic surfactants, the same puzzling phenomenon was encountered. For example, for mixed $C_{12}NE$-$C_{12}S$ systems, viscoelasticity can be observed only when $C_{12}S$ is in excess. The solutions with $C_{12}NE$ in excess show no viscoelasticity even though its viscosity is very high, such as 0.1 mol · dm^{-3}, 2 : 1 $C_{12}NE$-$C_{12}S$ solution, which is very viscous, but no elasticity can be observed.

As stated above, some viscoelastic solutions exhibit negative thixotropy and the negative thixotropic solutions are usually viscoelastic. The negative thixotropy may be likely induced by lamellar or sheet-like micelles. On this ground, we thought that, besides rodlike micelles, lamellar or sheet-like micelles might induce to viscoelasticity as well. For the lamellar or sheet-like micelles, the parallel arrangement form of bilayers is destroyed and turn to disordered when the solution is sheared, in the meantime, the system may store energy. There might be the tendency that the bilayers return to the parallel arrangement form when shearing is stopped, which may lead to the elasticity.

Since the large polar group of $C_{12}NE$ is unfavorable to the parallel arrangement of surfactant molecules the mixtures of $C_{12}NE$ and $C_{12}S$ are not easy to form lamellar micelles when $C_{12}NE$ is in excess. On the other hand, the lifetime of individual rodlike micelles formed when $C_{12}NE$ is in excess might be short, no permanent network could be formed. As a result, no elasticity could be observed when $C_{12}NE$ is in excess.

It could be seen from Fig. 2 that the viscoelastic solutions without negative thixotropy have concentrations lower than those with negative thixotropy. In other words, their micelles have lower charge density. Therefore, the viscoelastic solutions without negative thixotropy might have more poor stability, phase separation might occur on standing as a consequence of the growth and coagulation of micelles.

High viscosity of shear rate dependent

Another outstanding feature deviating from Newtonian behavior for the mixtures of cationic-anionic surfactants is the high viscosity at relatively low concentration. Some solutions are so viscous that they can almost not flow at normal conditions, such as 0.1 mol · dm^{-3}, 1 : 1.9 $C_{12}NE$-$C_{12}S$.

Using reduced-pressure capillary viscometer, the apparent viscosity was determined at different driving pressures. It shows that the high viscosity is shear rate dependent and the solution shows obvious shear thinning properties, no negative thixotropy was observed. A typical set of data is shown in Fig. 3.

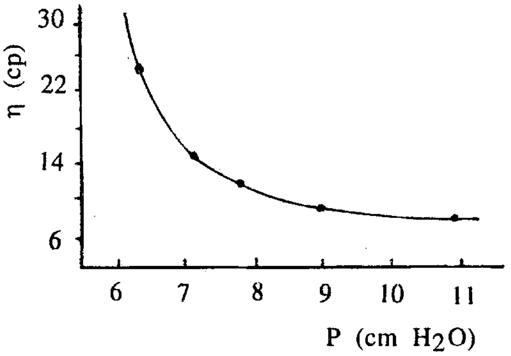


Fig. 3 Aparent viscosity of $C_{12}NE\text{-}C_{12}S$ 0.1 mol·dm^{-3}, 1:2, 25 °C

The phenomenon of high viscosity may be interpreted in terms of the existence of three dimension network formed by long rodlike micelles. The network is destroyed and the rodlike micelles move along the direction of shear stress when the solutions are sheared. As a result, the viscosity decreases with the increase of shear rate. This conclusion is in agreement with the data of Hoffmann et al. in which the highly viscosity and shear thinning properties observed with cetyltrimethylammonium bromide-salicylic acid (CTAB-SA) are interpreted in terms of the network of overlapping rodlike micelles [17–22].

Viscosity lowering with increasing concentration

It is a common understanding that viscosity increases with increasing concentration. However, for the aqueous mixtures of cationic-anionic surfactants, a converse change of viscosity could be observed. As state above, at the boundary between the mediate concentration region and the high concentration region, the mixtures of cationic-anionic surfactants usually exhibit viscoelasticity and negative thixotropy and, with the increase of concentration, viscoelasticity and negative thixotropy vanish gradually and the solutions became fluent and clear like water. Correspondingly, the viscosity initially decreases with increasing concentration, passes through a minimum, and then increases again. A typical set of date is shown in Table 3.

In another paper [7], we propose the model of rod (or lamella)-to-sphere transition of micelles. In this model, at relative high concentration, with the continuing increase of surfactant concentration, the micelle of mixed cationic-anionic surfactants undergo a transition from long to short rod, and then to spherical shape. In other words, at high concentration, micellar size decreases with increasing concentration. The sizes of micelles of 1:5 $C_{12}NE\text{-}C_{12}S$ at high concentration was measured by dynamic light scattering technique, which is shown in Table 3. It should be pointed out that, since the micelles in this system are charged highly, the strong interaction between charged micelles makes the formula by which the micelle sizes are calculated [6] not to fit this system quite well, the values in Table 3 should be regarded as the "apparent" micelle sizes. At any rate, the data in Table 3 do clearly show the relative size change during the rod (or lamella)-to-sphere transision of micelles. Therefore, the concetration-induced viscosity lowering might be considered as a result of the decrease of micellar size with the increase of concentration.

Table 3 Viscosity and micelle sizes of 1:5 $C_{12}NE\text{-}C_{12}S$ solution (25 °C)

Total concentration (mol·dm-3)	η* (cp)	Negative thixotropy**	Visco-elasticity	Micellar size *d*/*A*
0.10	1.07	No	No	20.0
0.05	0.98	No	No	21.0
0.01	0.90	No	No	49.0
8.0×10^{-3}	0.88	Yes	Yes	65.4
6.0×10^{-3}	0.96	Yes	Yes	70.9
5.0×10^{-3}	1.03	Yes	Yes	113.7
4.0×10^{-3}	1.06	Yes	Yes	186.8
3.0×10^{-3}***	–			

* η is the average viscosity over a range of P between 1.39 and 21.44 cm·H_2O column

** For negative thixotropic solutions, the viscosity is that at a time t = 0 (minimum viscosity)

*** Below 3.0×10^{-3} mol·dm^{-3}, precipitation or phase separation occurs

The rheological properties of the aqueous surfactant two-phase systems

When a cationic and a anionic surfactant solutions are mixed at certain concentration the solution separates spontaneously into two immiscible phases with a clear interfacial boundary between them [6, 11, 23]. Such a system may be coined as aqueous surfactant two-phase system (ASTP system). If it is formed when cationic surfactants are in excess, it is called ASTP-C system and when anionic surfactants are in excess it is called ASTP-A system. In ASTP-A systems, the two phases are called the water-like phase and oil-like phase respectively, not the upper and lower phases, since the positions of the two phases are changeable with temperature [11].

Tables 4–5 show the apparent viscosity (η) at different driving pressures (p) of the two phases. Table 6 shows the comparison of the rheological properties between ASTP-C and ASTP-A systems.

As can be seen, both the upper phases of ASTP-C systems and the water-like phases of ASTP-A systems are very viscous and shear thinning. The lower phases of

Table 4 Apparent viscosity of ASTP-C systems $C_{12}NE$-$C_{12}S$, 0.05 mol·dm^{-3}, 1.8 : 1

Upper phase											
P (cm H_2O)	46.19	51.69	59.59	64.36	65.49	71.29	77.09	79.86	84.89	95.20	110.55
η (cp)	17.41	15.68	13.15	12.56	11.68	10.76	10.09	9.98	9.27	8.45	7.49
Lower phase											
P (cm H_2O)			5.71		9.50		13.31		20.80		
η (cp)			0.93		0.91		0.91		0.92		

Table 5 Apparent viscosity of ASTP-A systems $C_{12}NE$-$C_{12}S$, 0.05 mol·dm^{-3}, 1 : 1.65

Water-like phase									
P (cm H_2O)	64.27	70.47	76.75	82.95	89.15	95.19	101.39	107.44	113.64
η (cp)	10.10	9.80	8.67	7.75	7.02	6.53	6.16	5.88	5.23
Oil-like phase									
P (cm H_2O)			7.43		10.61		13.47		19.51
η* (cp)			1.24		1.18		1.17		1.15

* The viscosity is that at a time $t = 0$ (minimum viscosity)

Table 6 Comparison of rheological properties of ASTP-C and ASTP-A systems of $C_{12}NE$-$C_{12}S$

	ASTP-C		ASTP-A	
	Upper phase	Lower phase	Water-like phase	Oil-like phase
Appearance	Very viscous	Very clear	Very viscous	Slightly viscous
Fluid type	Non-Newtonian Shear thinning	Newtonian	Non-Newtonian Shear thinning	Non-Newtonian
Viscoelasticity	No	No	No	Yes
Negative thixotropy	No	No	No	Yes

ASTP-C system are clear like water. The oil-like phases of ASTP-A systems are viscoelastic and negative thixotropic.

It is interesting to note that the ASTP-C systems, prior to phase separation, or shaken after phase separation, is turbid and not viscous, but from which a very viscous phase (the upper phase) could be separated out on standing. It is apparent that the turbid system of good fluidity would be an emulsion with the the upper phases as the dispersed phase.

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