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Interaction of nonionic surfactant AEO_9 with ionic surfactants*

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Abstract: The interaction in two mixtures of a nonionic surfactant AEO_9 ($C_{12}H_{25}O(CH_2CH_2O)_9H$) and different ionic surfactants was investigated. The two mixtures were AEO_9/sodium dodecyl sulfate (SDS) and AEO_9/cetyltrimethylammonium bromide (CTAB) at molar fraction of AEO_9, $\alpha_{AEO_9}=0.5$. The surface properties of the surfactants, critical micelle concentration (CMC), effectiveness of surface tension reduction (γ_{CMC}), maximum surface excess concentration (Γ_{max}) and minimum area per molecule at the air/solution interface (A_{min}) were determined for both individual surfactants and their mixtures. The significant deviations from ideal behavior (attractive interactions) of the nonionic/ionic surfactant mixtures were determined. Mixtures of both AEO_9/SDS and AEO_9/CTAB exhibited synergism in surface tension reduction efficiency and mixed micelle formation, but neither exhibited synergism in surface tension reduction effectiveness.

Key words: Nonionic surfactant, Nonionic-ionic mixed surfactants, Molecular interaction parameter, Synergism, Mixed micelle, Mixed adsorption film

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INTRODUCTION

Long chain nonionic surfactants such as polyoxyethylenated alcohols $C_{12}H_{25}O(CH_2CH_2O)_9H$ (AEO_9), are widely used in the chemical industry in fabric detergency and tertiary oil recovery due to their excellent surface-active properties. In many practical applications, surfactants are used in formulations containing mixtures of different compounds, and synergism can often be observed. Synergism is defined here as the condition in which the properties of a mixture are better than those attainable with the individual components separately. An important mixed system is that including ionic surfactants and nonionic surfactants (Gharibi *et al.*, 2000; Goloub *et al.*, 2000; Hou *et al.*, 2000; Maeda, 1995; Matsubara *et al.*, 2001; Rosen and Zhou, 2001; Shivaji Sharma *et al.*, 2003; Zana *et al.*, 1998).

This work aimed at investigating molecular interaction in two mixtures of nonionic surfactant AEO_9 with two different ionic surfactants and at searching for synergism. In this paper, sodium dodecyl sulfate (SDS) and cetyltrimathylammonia bromide (CTAB) were chosen as the components for the two mixtures studied: AEO_9/SDS and AEO_9/CTAB.

EXPERIMENTAL DETAILS

Materials

AEO_9 was obtained from Zhejiang Huangma Co., Ltd. SDS was procured from Fluka Chemical Co. and was recrystallized three times from mixed solvents of water and ethanol before use. CTAB was obtained from Nanjing Robiot Co., Ltd. and was recrystallized three times from mixed solvents of acetone and ethanol before use. Water was deionized and doubly distilled.

Surface tension measurements

The critical micelle concentration (CMC) values

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of the surfactants were determined from the surface tension isotherms as per the National standard of the PRC "Anionic and non-ionic surface active agents−The critical micellization concentration was determined by measuring surface tension with the ring" GB/T 11278-1989 test method. The surface tension, γ, of aqueous solutions of the surfactants was measured by using a JYW 2000A automatic tensiometer equipped with a du Nouy Pt-Ir ring. The measurements were performed at 20 °C. Sets of measurements were taken until no significant change of tension occurred.

RESULTS AND DISCUSSION

Surface properties of the surfactants mixtures

The relationships of surface tension vs log molar concentration for the two mixtures of AEO₉/SDS and AEO₉/CTAB at $\alpha_{\mathrm{AEO_9}}$=0.5 are shown in Fig.1 and Fig.2, where $\alpha_{\mathrm{AEO_9}}$ is the molar fraction of AEO₉ in the total surfactant in the solution phase. The surface tension data allow us to calculate the maximum surface excess concentration, $\Gamma_{\max}$, at the air/water interface based on the Gibbs adsorption equation

$$\mathrm{d}\gamma/\mathrm{d}\ln a = -RT\Gamma_{\max} \quad (1)$$

where R=8.314 J/(mol·K), γ is the surface tension in mN/m, T is absolute temperature, a is the activity (at low surfactant concentration may be replaced by concentration). Surface excess may be determined from the slope of the surface tension isotherm.

The average minimum area per molecule ($A_{\min}$) occupied by one compound molecule in the surface layer (assuming the layer is monomolecular) can be obtained from the equation

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

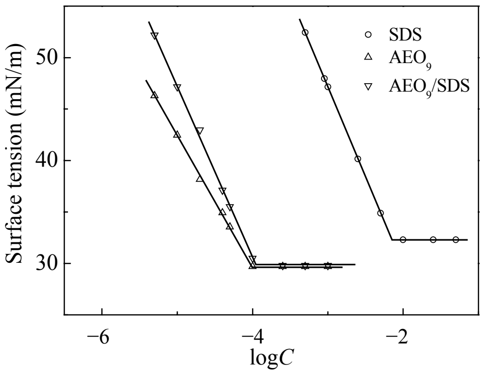

Fig.1 Surface tension isotherms for mixture of AEO₉/SDS ($\alpha_{\mathrm{AEO_9}}$=0.5), AEO₉ and SDS

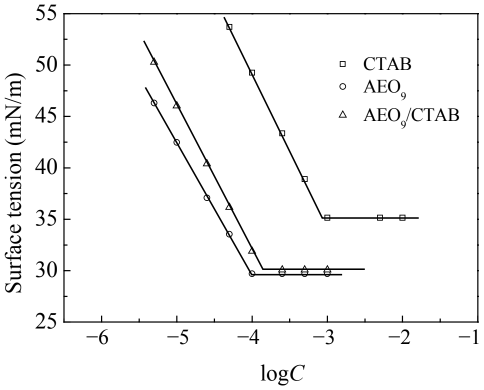

Fig.2 Surface tension isotherms for mixture of AEO₉/CTAB ($\alpha_{\mathrm{AEO_9}}$=0.5), AEO₉ and CTAB

where N_A is Avogadro constant. The values of CMC, γ_{CMC} (the surface tension at the CMC), $\Gamma_{\max}$ and $A_{\min}$ of these mixtures obtained in this way are presented in Table 1 together with those of individual surfactants. Larger surface activity (values of larger $\Gamma_{\max}$, smaller CMC) of the AEO₉/SDS mixture than that of the AEO₉/CTAB mixture is apparent.

Surfactant-surfactant interaction

The nature and extent of the interaction between the two different surfactant molecules can be measured by the molecular interaction parameters β, which

Table 1 Surface properties of AEO₉/SDS and AEO₉/CTAB mixtures ($\alpha_{\mathrm{AEO_9}}$=0.5) and individual surfactants

System	*CMC* (mol/m^3)	γ_{CMC} (mN/m)	$\Gamma_{\max}$ (10^{-6} mol/m^2)	$A_{\min}$ (10^{-20} m^2)	Ideal $A_{\min}$ (10^{-20} m^2)
AEO₉/SDS	0.11	29.8	3.0	56	71
AEO₉/CTAB	0.135	30.1	2.5	66	72
AEO₉	0.10	29.7	2.3	73	
SDS	7.0	32.3	3.1	53	
CTAB	0.90	35.1	2.6	63	

can be evaluated using Eqs.(3)–(6), which are based upon the application of nonideal solution theory to the thermodynamics of the system (Rosen, 1989). Negative β values indicate attractive interaction and positive values, repulsive interaction. The molecular interaction parameter for mixed adsorption film formation at the air/water interface, β^σ, is calculated by using the following equations (Li and Zhao, 2003; Rosen, 1989; Zhao, 1991).

$$\frac{(X_1^\sigma)^2\ln[(\alpha_1 C_{12}^0/C_1^0)^{1+k_1}/X_1^\sigma]}{(1-X_1^\sigma)^2\ln\{[(1-\alpha_1)C_{12}^0/C_2^0]^{1+k_2}/(1-X_1^\sigma)\}}=1 \quad (3)$$

$$\beta^\sigma=\frac{\ln[(\alpha_1 C_{12}^0/C_1^0)^{1+k_1}/X_1^\sigma]}{(1-X_1^\sigma)^2} \quad (4)$$

where α_1 is the molar fraction of surfactant 1 in the total surfactant in the solution phase; X_1^σ is the molar fraction of surfactant 1 in the total surfactant in the mixed adsorption film; k_1 and k_2 are the counterion association degree on the micelle of surfactants 1 and 2; C_1^0, C_2^0, and C_{12}^0 are the solution phase molar concentrations of surfactants 1, 2 and their mixture, respectively, required to produce a given surface tension value.

Similarly, the value of β^m, the interaction parameter for mixed micelle formation in an aqueous solution, is calculated from the following two equations (Rosen, 1989; Li and Zhao, 2003; Zhao, 1991)

$$\frac{(X_1^m)^2\ln[(\alpha_1 C_{12}^m/C_1^m)^{1+k_1}/X_1^m]}{(1-X_1^m)^2\ln\{[(1-\alpha_1)C_{12}^m/C_2^m]^{1+k_2}/(1-X_1^m)\}}=1 \quad (5)$$

$$\beta^m=\frac{\ln[(\alpha_1 C_{12}^m/C_1^m)^{1+k_1}/X_1^m]}{(1-X_1^m)^2} \quad (6)$$

where X_1^m is the molar fraction of surfactant 1 in the total surfactant in the mixed micelle; C_1^m, C_2^m, and C_{12}^m are the critical micelle concentrations of individual surfactants 1 and 2, and their mixture, respectively, at a given value of α_1. Eq.(3) (or Eq.(5)) is solved iteratively for X_1^σ (or X_1^m) and substitution of this in Eq.(4) (or Eq.(6)) yields the value of β^σ (β^m).

In this paper, surfactant 1 is AEO$_9$ and surfactant 2 is CTAB or SDS. From literature (Rosen, 1989; Li and Zhao, 2003; Zhao, 1991), we had k_{SDS}=0.67, $k_{\mathrm{AEO_9}}$=0 and k_{CTAB}=0.67. Data of the β values for the two mixtures are listed in Table 2. As seen from the tabulated data, both β^σ and β^m values are negative, showing attractive interaction between these surfactant molecules. The larger β^σ and β^m values for the AEO$_9$/SDS mixture than those for the AEO$_9$/CTAB mixture indicate attractive interaction in the AEO$_9$/SDS mixture larger than that in the AEO$_9$/CTAB mixture.

For the mixed system, if there is no interaction between the two components composing the mixed adsorption film, the ideal molecular cross-sectional area of the mixed adsorption film can be calculated by the following equation (Rosen and Sulthana, 2001)

$$A_{\min}(\text{ideal})=X_1^\sigma\times A_{\min,1}+(1-X_1^\sigma)\times A_{\min,2} \quad (7)$$

where $A_{\min,1}$ and $A_{\min,2}$ are the cross-sectional areas per molecule of the first individual surfactant and the second surfactant, respectively, and X_1^σ is the molar fraction of surfactant 1 in the mixed adsorption film. The observed value ($A_{\min}$) and ideal mixing value (ideal $A_{\min}$) are given in Table 1. The data revealed that the mixtures of AEO$_9$/SDS and AEO$_9$/CTAB both have an $A_{\min}$ value considerably lower than the value obtained upon ideal mixing. The lowered $A_{\min}$ value indicates a significant attractive interaction between the two components in the two mixtures. This fact is reflected in the β^σ and β^m values obtained for the two mixtures. The deviation from ideal mixing, in general, increases with increasing difference between the head group cross-sectional areas (Bergström and Eriksson, 2000). Thus, the interaction in the AEO$_9$/SDS mixture being greater than that in the AEO$_9$/CTAB mixture reflects that the difference in the cross-sectional area between the two components

Table 2 Molecular interaction and synergism parameters for AEO$_9$/SDS and AEO$_9$/CTAB mixtures ($\alpha_{\mathrm{AEO_9}}$=0.5)

Mixture	β^σ	X^σ	$\ln(\frac{C_1^0}{C_2^0})$, A	β^m	X^m	$\ln(\frac{C_1^m}{C_2^m})$, B	$\beta^\sigma-\beta^m$	$A-B$
AEO$_9$/SDS	−7.2	0.92	5.1	−10.0	0.805	4.2	2.8	0.9
AEO$_9$/CTAB	−4.0	0.91	3.3	−4.3	0.8	2.2	0.3	1.1

in the former is larger than that in the latter.

Table 2 shows that the molar fraction of AEO_9 in bulk solution is smaller than that in the mixed micelles and the mixed adsorption film. From the structure of the two surfactants (AEO_9 and SDS or CTAB) and the micellar character, it appears that incorporation of SDS or CTAB into AEO_9 micelles is favored over incorporation of AEO_9 into SDS or CTAB micelles.

The compositions of the mixed adsorption film and the mixed micelle for the two mixtures obtained by Eq.(3) and Eq.(5) are approximately kept at 9:1 and 4:1 molar ratio for AEO_9:SDS or CTAB, indicating that the major portion of higher surface active AEO_9 molecules is continuously rearranged in these aggregates.

Synergism

The existence of synergism in mixtures containing two surfactants has been shown to depend not only on the strength of the interaction between them (measured by the values of the β parameter) but also on the relevant properties of the individual surfactant components of the mixture. Thus, the conditions for synergism in surface tension reduction efficiency (when the total concentration of the mixed surfactant required to reduce the surface tension of the solvent to a given value is less than that of either individual surfactant) are as follows: (a) β^σ must be negative and (b) $|\beta^\sigma|>|\ln(C_1^0/C_2^0)|$ (Rosen, 1989). From data in Table 2, it is apparent that the AEO_9/SDS mixture exhibits synergism in surface tension reduction efficiency, since the β^σ value is −7.2 and the $|\ln(C_1^0/C_2^0)|$ value is 5.1. The AEO_9/CTAB mixture also exhibits synergism in surface tension reduction efficiency, since the β^σ value is −4.0 and the $|\ln(C_1^0/C_2^0)|$ value is 3.3.

Synergism in the mixed micelle formation exists when the CMC of a mixture is less than that of individual surfactants among the mixture. The conditions for synergism to exist in the mixture are as follows: (a) β^m must be negative; (b) $|\beta^m|>|\ln(C_1^m/C_2^m)|$ (Rosen, 1989). The mixture of AEO_9/SDS exhibits synergism in mixed micelle formation, since the β^m value is −10.0 and the $|\ln(C_1^m/C_2^m)|$ value is 4.2. The mixture of AEO_9/CTAB also exhibits synergism, since the β^m value is −4.3 and the $|\ln(C_1^m/C_2^m)|$ value is 2.2.

Synergism in surface tension reduction effectiveness (when the surface tension of the mixture at its CMC is lower than that of the individual surfactants at their respective CMC) depends upon the value of both β^σ and β^m, in addition to the C_1^0, C_2^0, C_1^m and C_2^m values of the two surfactants. The conditions for this type of synergism to exist are (a) ($\beta^\sigma-\beta^m$) must be negative; (b) $|\beta^\sigma-\beta^m|>|\ln(C_1^0C_2^m/C_2^0C_1^m)|$ (Rosen, 1989). The two mixtures of AEO_9/SDS and AEO_9/CTAB does not exhibit this type of synergism, since ($\beta^\sigma-\beta^m$) is positive (Table 2).

CONCLUSION

Interaction in two mixtures of a nonionic surfactant AEO_9 ($C_{12}H_{25}O(CH_2CH_2O)_9H$), and sodium dodecyl sulfate (SDS) or cetyltrimethylammonium bromide (CTAB) at α_{AEO_9}=0.5 were investigated. The conclusions were as follows:

1. The AEO_9/SDS and AEO_9/CTAB mixtures both exhibit synergism in surface tension reduction efficiency and mixed micelle formation, whereas neither exhibits synergism in surface tension reduction effectiveness.
2. The AEO_9/SDS and AEO_9/CTAB mixtures both show packing contraction at the air/water interface, and the former mixture has larger surface activity.

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