

Location of ethanol in sodium dodecyl sulfate aggregates

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The hexagonal liquid crystalline phase of SDS (Sodium dodecyl sulfate)/H₂O system changes into lamellar liquid crystal and the effective length of surfactant molecule $d_0/2$ in the lamellar liquid crystal decreases with the addition of ethanol. The micellar aggregation number N of SDS decreases and the micellar diffusion coefficient increases with the added ethanol. Under a constant concentration of SDS, the molecule number ratio of ethanol to SDS in the micelle increases with the concentration of ethanol and even exceeds 10 when ethanol concentration is 1.085 mol/L. All these results show that ethanol, even though a short chain alcohol and soluble in water, can partly exist in the interphase of the amphiphilic aggregates showing some properties of co-surfactant.

Keywords Ethanol, hexagonal liquid crystal, lamellar liquid crystal, micelle, aggregation number, diffusion coefficient

Introduction

Co-surfactant plays an important role in the amphiphilic self-assembly systems.^{1,2} In most cases co-surfactant is an alcohol with medium chain length (*e. g.* butanol to hexanol). In these cases, co-surfactants exist in the interphase of self-assembled aggregates, decreasing the interaction between polar heads of the amphiphilic molecules, thus stabilizing the aggregates.

Ethanol is a short chain alcohol and soluble in water. In micelle systems, it is generally thought to be adsorbed in the interface of the micelle and exists in water continuous phase instead of being located in the micelle interphase. Hence, under most circumstances, ethanol is not used as co-surfactant in the amphiphilic self-assembly systems with water as solvent and the location of ethanol in the amphiphilic self-assembly systems is seldom mentioned.

Our research is based on SDS/C₂H₅OH/H₂O system and is carried out in five aspects: the partial phase diagram, structure of lamellar liquid crystal, aggregation number of SDS micelle, molecule ratio of ethanol to SDS in the interphase and the diffusion coefficient D_0 of the micelle. All our results give out one conclusion that in the system of SDS/C₂H₅OH/H₂O, although the majority of ethanol is dissolved in water continuous phase and some part of ethanol is adsorbed in the interface of the amphiphilic self-assembled aggregates, there is still some part of ethanol existing in the interphase of the self-assembled aggregates.

Experimental

Materials

Sodium dodecyl sulfate (SDS, Sigma, 98%) was recrystallized twice from ethanol. Ethanol was from Aldrich (99%). Pyrene was from Aldrich (99%) and cetylpyridine chloride from Fluka (98%). Water used was twice distilled.

Partial phase diagram

The isotropic solution region of SDS/C₂H₅OH/H₂O was determined by titrating ethanol into the mixture of SDS and water with various ratios, or titrating water in the mixture of SDS and ethanol. The hexagonal and lamellar liquid crystal regions of SDS/C₂H₅OH/H₂O were determined in the same way with isotropic solution region. The boundary line was checked with an optical microscope with polarized light (Model 59X from Shanghai Analytical Instrument Factory) and by low angle X-

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ray diffraction.

Low angle X-ray diffraction

Low angle X-ray diffraction measurements were obtained from D/maxrc X-ray diffractometer (Rigaku, Japan). Ni filter and Cu radiation (wavelength = 0.1542 nm) were used.

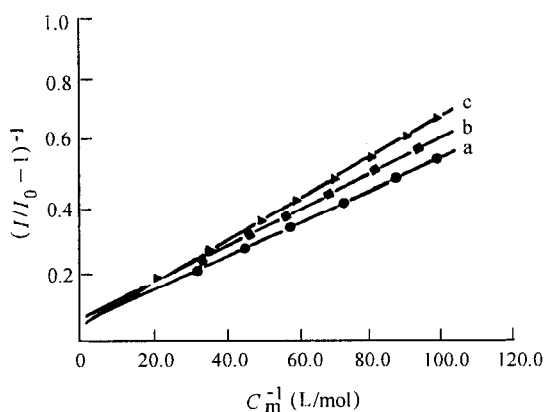


Fig. 1 Relation between $(I/I_0 - 1)^{-1}$ and C_m^{-1} . The concentration of ethanol is (a) 0.17 mol/L, (b) 0.34 mol/L, and (c) 0.68 mol/L.

Determination of binding constant K

In the isotropic solution of surfactant, water and additive, there exists an equation as follows:³

$$(I/I_0 - 1)^{-1} = (I_m/I_0 - 1)^{-1}(1 + 1/\nu KC_m) \quad (1)$$

where I is the fluorescence intensity at various SDS concentration, I_0 is the fluorescence intensity without SDS, I_m is the maximum fluorescence intensity, K is the binding constant of additive with the micelle. For a definite system, $\nu = 1$. C_m is the surfactant concentration to form micelles and is equal to

$$C_m = C_t - CMC \quad (2)$$

C_t is the total surfactant concentration and CMC the critical micellar concentration. The relationship between $(I/I_0 - 1)^{-1}$ and C_m^{-1} was shown in Fig. 1. From the slope and the intercept of the curve, the binding con-

stant K can be obtained. In the measurement of fluorescence intensity, the optimum emission wavelength was 380–420 nm and the optimum excitation wavelength was 346 nm. Model RF-540 fluorescence spectrometer (Rigaku, Japan) was used.

Determination of micellar aggregation number N

The aggregation number N of SDS micelle was determined by measuring the total intensity of fluorescence with and without quencher, $I(t)$ and $I(0)$, respectively. According to the following equation:⁴

$$I(t) = I(0) \exp(-[Q]/[M]) \quad (3)$$

where $[Q]$ is the concentration of quencher and $[M]$ the micelle concentration, which is related to N by

$$[M] = ([st]) - [sf]/N \quad (4)$$

where $[st]$ is the total concentration of surfactant, $[sf]$ is the concentration of monomer surfactant and to a good approximation can be taken as the CMC . Combining Eqs. (3) and (4)

$$\ln[I(t)/I(0)] = N[Q]/(CMC - [st]) \quad (5)$$

From a plot of $\ln[I(t)/I(0)]$ against $[Q]$, N can easily be calculated from the slope of the straight line. In this measurement, the excitation wavelength is 335 nm and the emission wavelength is 380–420 nm. CMC values are determined by measurements of conductivity under DDS-11A conductometer (Second Analytical Instrument Factory of Shanghai).

Determination of diffusion coefficient

Electrochemical measurements are conducted in a three-electrode configuration with platinum as the working electrode, platinum plate as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. After a continuous flow of nitrogen, the cyclic voltammogram for SDS solution can be obtained at platinum electrode with the swept potential (Fig. 2).

All of our measurements are carried out at $25 \pm 0.1^\circ\text{C}$.

Results and discussion

Partial phase behaviors of SDS/C₂H₅OH/H₂O system

Fig. 3 shows the partial phase diagram of SDS/C₂H₅OH/H₂O system. There is an isotropic solution region L, a hexagonal liquid crystal region Hex and a lamellar liquid crystal region LLc.

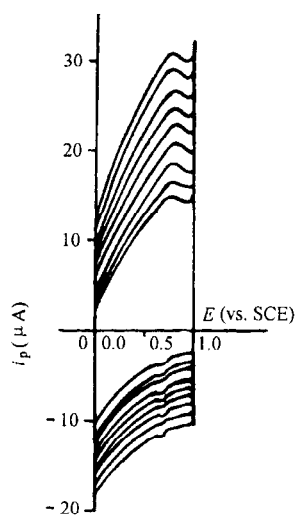


Fig. 2 Cyclic voltammogram at different potential sweep rates in 0.018 mol/L SDS aqueous solution.

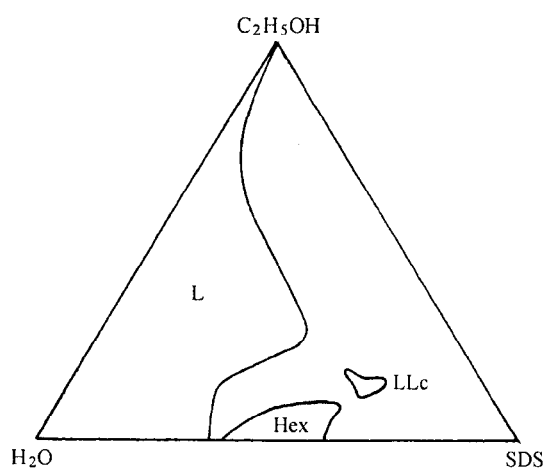


Fig. 3 Partial phase diagram of SDS/C₂H₅OH/H₂O system. L is isotropic solution region, Hex is hexagonal liquid crystal region and LLc is lamellar liquid crystal region.

Since ethanol is soluble in water, the isotropic solution region is large. Normal hexagonal liquid crystal is formed in the mixture of SDS/H₂O from water contents 41% to 61%. Ethanol can be dissolved in the hexagonal liquid crystal, but this dissolution causes a reduction of hexagonal liquid crystal region. When the ethanol content is higher than 9%, hexagonal liquid crystal region disappears. In SDS/H₂O system, when the content of SDS is between 67% and 77%, the system is the mixture of hexagonal and SDS. The addition of ethanol to the system results in the formation of lamellar liquid crystal. These results suggest that there are some ethanol existing in the interphase of the hexagonal liquid crystal and the lamellar liquid crystal. Only in this way can the addition of ethanol reduce the hexagonal phase region and transform the hexagonal phase to lamellar phase.

Low angle X-ray measurements provide another evidence for location of ethanol in the lamellar liquid crystal (Fig. 4). Value d_0 shows twice the length of the effective length of surfactant in the amphiphilic bilayer of lamellar liquid crystal. As Fig. 4, d_0 is about 2.4—2.5 nm in the lamellar crystal of SDS/C₂H₅OH/H₂O system.

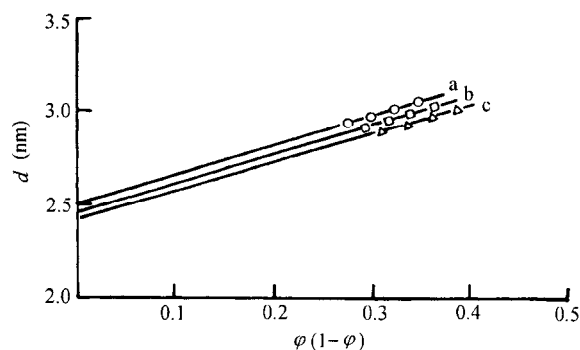


Fig. 4 Relation between interlayer spacing d and water content ϕ . C₂H₅OH/SDS (wt/wt) is: (a) 18/82, (b) 21/79 and (c) 23/77.

The effective length l of surfactant molecules in the associated structure can be theoretically calculated from the following equation:⁵

$$l = 0.95 \times (1.5 + 1.265n) \quad (6)$$

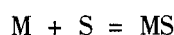
in which the constant (0.95) is the reflection of the disorder of hydrocarbon chains in amphiphilic bilayer. n is

the carbon number of surfactant. For SDS, $n = 12$, so $l = 1.58$ nm. Comparing with the values of $d_o/2$ shown in Fig. 4, which are 1.2—1.25 nm, we can see that the addition of ethanol decreases the effective length of SDS molecules. This result implies that some ethanol molecules are located between the SDS molecules in the amphiphilic bilayer of lamellar liquid crystal and thus reduce the order degree of SDS molecules. With reduced order degree, SDS molecules bend to some extent and their effective length thus decreases.

Molecule ratio of ethanol to SDS in the micelle

The measurement of the molecule ratio of ethanol to SDS (r) can provide us with another clue to the location of ethanol in SDS aggregation system.

In the system of SDS/C₂H₅OH/H₂O, there exists such an equilibrium⁶ with K as binding constant:



where M is micelle, S is ethanol free in water continuous phase and MS represents ethanol bound to micelles. The distribution coefficient of ethanol between the water continuous phase and micelle phase, P_{mw} , can be related to binding constant K by the following equation:⁷

$$K = (P_{mw} - 1) V_0 \quad (7)$$

where V_0 is the partial volume of SDS, $V_0 = 0.246$ L/mol⁸ above CMC of SDS. P_{mw} can also be expressed by the follows:⁹

$$P_{mw} = (1 - q) M_m / q M_{aq} \quad (8)$$

where $q = VC_m$ is the volume fraction of micelle phase system. M_m and M_{aq} are the molar fraction of ethanol associated with micelle and free in water phase, respectively. Assuming

$$p = M_m / M_{aq} \quad (9)$$

$$\text{so} \quad P_{mw} = (1 - q) p / q \quad (10)$$

$$\text{Since} \quad M_m + M_{aq} = 1$$

$$M_m = p / (1 + p) \quad (11)$$

Hence, the molecule ratio of ethanol to SDS in the micelle, r , is as follows:

$$r = M_m C_o / C_m = p C_o / (1 + p) C_m \quad (12)$$

where C_o is the total concentration of ethanol and C_m is the micellar concentration. Fig. 5 shows the variation of r with C_m . The results in Fig. 5 show that under a constant concentration of ethanol, the molecule ratio of ethanol to SDS, r , decreases with the concentration of SDS. The data also show that under a constant concentration of SDS, the molecule ratio, r , increases with the concentration of ethanol and even exceeds 10 when ethanol concentration is 1.085 mol/L (curve d). This result suggests that each SDS molecule is associated with at least ten ethanol molecules in the micelle phase. Obviously, it is impossible for all these ethanol molecules to exist only by the way of being adsorbing in the interface of the micelle. As we can deduce, some ethanol molecules must have existed in the interphase of the micelle.

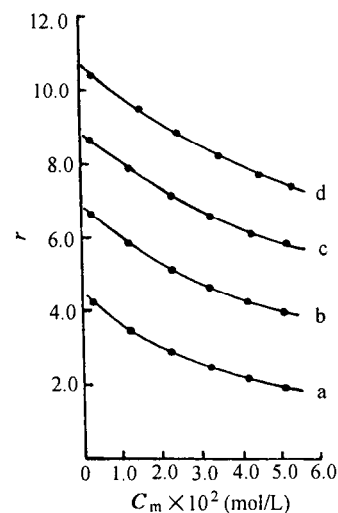


Fig. 5 Relation between molecule number ratio of ethanol to SDS in the micelle r and the surfactant concentration to form micelle C_m . The total concentration of ethanol C_o is: (a) 0.17 mol/L, (b) 0.34 mol/L, (c) 0.86 mol/L and (d) 1.085 mol/L.

Micellar aggregation number N

The obvious decrease of the aggregation number N

of SDS micelle system with the addition of ethanol can further prove our idea about the location of ethanol (Table 1).

The decrease of micelle aggregation number N with the addition of ethanol can be explained by the length of the hydrophobic group lc of the surfactant molecule, the cross-sectional area of the hydrophilic group a_o and the volume of hydrophobic group v_H . For spherical micelle, N can be expressed as follows:¹⁰

$$N = 4\pi(lc + s)^2 / a_o \quad (13)$$

$$N = 4\pi(lc)^3 / 3v_H \quad (14)$$

where s is the added length of the radius of the sphere due to the hydrophilic group. It is obvious that the aggregation number N will increase with the length of the hydrophobic group lc of the surfactant molecule and decrease with increase in the cross-sectional area of the hydrophilic group a_o and the hydrophobic group volume v_H . The decrease of the aggregation number N of SDS micelle system (Table 1) shows that the addition of ethanol can increase the value of a_o or v_H . But the only way for ethanol to increase a_o or v_H is to exist in the interphase of the micelle. The result is corresponding to our former conclusions.

Diffusion coefficient of SDS micelle system

The location of ethanol in the micelle phase directly affects the diffusion coefficient of SDS micelle as determined by the cyclic voltammogram.

Fig. 2 shows that cathodic peak potential E_p is independent of the sweep rate, and Fig. 6 shows that cathodic peak current i_p is proportional to the square root of potential sweep rate which indicates diffusion control.¹¹ Thus the electrochemical progress of SDS micelle solution is reversible. The mechanism of the electrochemical reaction for SDS at platinum electrode can be obtained by rotating ring-disk electrode (RRDE).^{12,13}

For a reversible wave, the relationship of the peak current i_p with potential rate ν , solution concentration C_o and diffusion coefficient D_o at 25°C is as follows:¹¹

$$i_p = 2.69 \times 10^5 n^{3/2} C_o D_o^{1/2} \nu^{1/2} A \quad (15)$$

Cathodic peak current i_p is in amperes, solution concentration C_o in mol/cm³, potential sweep rate ν in V/s, particle diffusion coefficient in the solution D_o in cm²/s, area of electrode A in cm².

The number of electrons per SDS molecule oxidized or reduced, n , can be calculated from peak potential E_p and half-peak potential $E_{p/2}$. The relationship between E_p , $E_{p/2}$ and n is as follows:¹¹

$$|E_p - E_{p/2}| = 2.2RT/nF \quad (16)$$

For SDS reaction at platinum electrode, $n = 1$ approximately (Table 2). Thus from Eq. (15), we can get the diffusion coefficient of SDS aggregates.

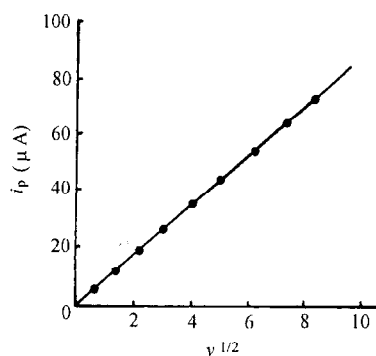


Fig. 6 Peak currents with the square root of potential sweep rates.

We have measured the diffusion coefficient of SDS micelle solution without ethanol in our former research and obtained the first and the second CMC as 8.0×10^{-3} mol/L and 5.6×10^{-2} mol/L, respectively.¹² When SDS concentration is smaller than the first CMC , SDS exists in the structure of monomer molecules or premicelles. The results in Fig. 7 show that under such a circumstance, the addition of ethanol only leads to a slight increase of SDS diffusion coefficient. So the slope of line (a) is only 0.22 (Fig. 7). When SDS concentration is between the first and the second CMC , SDS exists as spherical micelle.¹³⁻¹⁹ The diffusion coefficient of spherical micelles is smaller than that of monomer molecules or premicelles because the volume of spherical micelles is greater than that of monomer molecules or premicelles, so line (b) is below line (a). With the increasing ethanol concentration, the diffusion coefficient of spherical micelles increases faster than that of monomer

molecules or premicelles and so the slope of line (b) is 0.4 and is twice that of line (a). This result proves that some added ethanol is located in the interphase of the spherical micelle and results in the decrease of aggregation number, hence the increase of diffusion coefficient. When SDS concentration is higher than the second CMC, the shape of the micelle is rod-like.¹³⁻¹⁹ The volume of rod-like micelles is larger and the diffusion coefficient is smaller than that of spherical micelles, as a result, line (c) is below line (b). Meanwhile, the slope of line (c) is larger than that of line (b) and is approximately 0.62. This result again implies that some part of the ethanol exists in the interphase of the rod-like micelle and results in the micelle disaggregation to some extent, hence the increase of the diffusion coefficient.

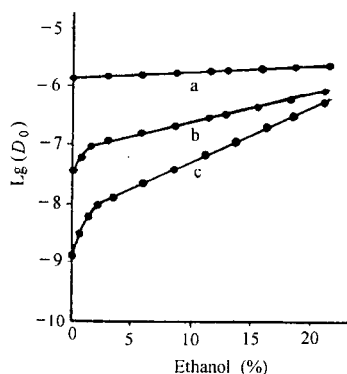


Fig. 7 Logarithm of diffusion coefficient of micelle with ethanol concentration (weight percent) in SDS solution. (a) 0.0018 mol/L, (b) 0.018 mol/L and (c) 0.18 mol/L SDS solution.

Conclusion

In the present research, we have demonstrated the location of ethanol in SDS aggregates system from five aspects: a) The addition of ethanol can reduce the hexagonal region and transform the normal hexagonal liquid crystal to lamellar liquid crystal; b) the effective length of surfactant which is shown by half of the inter-layer space of the lamellar liquid crystal is much less than the theoretical value; c) the molecule ratio of ethanol to SDS, r , in the micelle increases with ethanol content and even exceeds 10 under the certain conditions; d) the addition of ethanol greatly decreases the aggregation number N of SDS micelle; e) the diffusion coefficient of SDS micelle decreases with the addition of

ethanol. The combination of the above results gives out the conclusion that some ethanol can exist in the interphase of the SDS aggregates in addition to being adsorbed. Thus, ethanol, though a short chain alcohol, can also act as a co-surfactant in SDS aggregate system.

Table 1 Micellar concentration $[M]$, aggregation number N , binding constant K and distribution coefficient P_{mw} at different ethanol concentration

$C_{C_2H_5OH}$ (mol/L)	$[M](10^4)$ (mol/L)	N	K	P_{mw}
2.0×10^{-4}	2.56	55	60	245
2.5×10^{-4}	2.60	54	52	211
1.0×10^{-4}	2.63	54	46	188
5.0×10^{-3}	2.71	52	42	172
1.0×10^{-2}	2.87	49	38	156
0.17	3.40	40	26	106
0.34	4.2	34	20	82
0.68	6.2	23	13	54
0.86	7.1	20	11	48

Table 2 Potential sweep rate ν , peak potential E_p , half-peak potential $E_{p/2}$ and electrons per molecule oxidized or reduced n

No.	ν (mV/s)	E_p (V)	$E_{p/2}$ (V)	n
1	6.0	0.71	0.65	0.93
2	12.0	0.70	0.64	0.95
3	18.0	0.70	0.64	0.95
4	24.0	0.69	0.63	0.97
5	30.0	0.70	0.65	0.97
6	36.0	0.70	0.65	0.97
7	42.0	0.69	0.63	0.96
8	48.0	0.69	0.63	0.96

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