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Sodium hexadecanoate micellar aggregation number

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Abstract: The diffusion coefficient of sodium hexadecanoate micelles was studied by polarography at 63 °C, and the size and aggregation number of the micelles was computed. At concentrations above 0.01 mol · L^{-1} rodlike micelles exist, which become flexible at 0.040 mol · L^{-1} and entangle at 0.043 mol · L^{-1}

Key words: Sodium hexadecanoate – Rodlike micelles – Diffusion Coefficients – Polarography – Micelle size

Introduction

Because of their high Krafft point and the possibility of using more soluble and less hydrolysable surfactants, sodium hexadecanoate micelles have not been extensively studied in the past. There is very little information in the literature about the size, shape, and aggregation number of micelles of this surfactant.

Some interest in methods for micelle size characterization have led to the use of polarographic techniques to estimate micelle diffusion coefficients via the redox behavior of associated electroactive probes [1–4]. These studies assumed that the presence of a small number of these probes per micelle will not affect its size and shape [5]. Polarographic methods have been successfully used to study the nature of concentrated microemulsions [6] and to determine the solubilisation site of electroactive probes in cationic micelles [7]. Polarographic techniques give – micelle self-diffusion coefficients, which are amenable to interpretation in terms of micelle shape and size. Besides, the self-diffusion coefficient is the kinetic entity one for the micelle, without its ionic atmosphere. We have applied the polarographic method to study the sodium hexadecanoate-water system.

Experimental

Solutions were prepared by weighing the appropriate amount of hexadecanoic acid (Fluka) in a volumetric flask. NaOH aqueous solution was added just to neutralize the acid, then a CdI_2 aqueous solution was added to tag the micelles and water was poured in to obtain the desired volume. The flask was heated to about 65 °C and then sonicated for 1 h in a Bransonic Ultra sonic Cleaner B-220 at 55 kHz to homogenize the system.

All solutions were prepared with double-distilled water.

Polarographic measurements were performed in a Radiometer PO4 polarograph, following the technique of Novodoff et al. [3]. Solutions were thermostatted to 63 °C; the Krafft point is 62 °C [8]

The Ilkovic equation was used, in the form.

$$i_d\ (\mu A) = 607 v D^{1/2} c m^{2/3} t^{1/6}\ , \qquad (1)$$

where i_d is the average diffusion current in microamperes, v is the number of electrons consumed in the reduction of the probe ($v = 2$), D is the kinetic entity self-diffusion coefficient and c the probe concentration, m is the rate of flow of mercury through the capillary, and t is the time elapsed between the fall of two consecutive mercury drops. This equation may be written in the

following way:

$$i_d = KcD^{1/2}\,, \tag{2}$$

and K may be obtained from the slope of i_d vs. Cd^{+2} concentration plot (Fig. 1). The Cd^{2+} diffusion coefficient was estimated as $D = 1.37 \times 10^{-9}\ m^2 s^{-1}$ at 63 °C by using the relations [9]:

$$D = ukT/eZ \tag{3}$$

$$u \cdot \eta = \text{constant} = 0.04763\ cm^2 \cdot V^{-1} Pa\,, \tag{4}$$

where k is the Boltzman constant, T the absolute temperature, η the viscosity of the medium (water), u, the ionic mobility, e the elementary charge, and Z the valence of the diffusing species. We used $D_{cd+2} = 6.9 \times 10^{-10}\ m^2\,s^{-1}$ at 25 °C [10] and η at 25° and 63 °C computed by the equation [11]:

$$\log(\eta_{20}/\eta_t) = \frac{1.37023(t-20) + 8.36 \times 10^{-6}(t-20)}{109 + t}\,, \tag{5}$$

where t is the temperature in °C and $\eta_{20} = 0.8909 \times 10^{-3}\ kg \cdot m^{-1} s^{-1}$.

The runs of sodium hexadecanoate solutions were made under the same conditions as those shown in Fig. 1, including the Cd^{2+} concentration range used as a tag. No additional supporting electrolyte was added.

From Eq. (2) the micelle diffusion coefficient D_M was obtained, and from the Stokes–Einstein equation, the hydrodynamic radius R_H was found:

$$D = \frac{kT}{6\pi\eta R_H}\,. \tag{6}$$

When error estimations were made, the confidence level was 0.90.

Results and discussion

Table 1 shows the measured sodium hexadecanoate solution data.

The determined hydrodynamic radii are incompatible with spherical micelles. The maximum radius for spherical micelles is approximately equal to the surfactant molecule length b, which may be computed by the equation [12]:

$$b(\text{nm}) = 0.13n_c + 0.1704 + 24_{ph}\,, \tag{7}$$

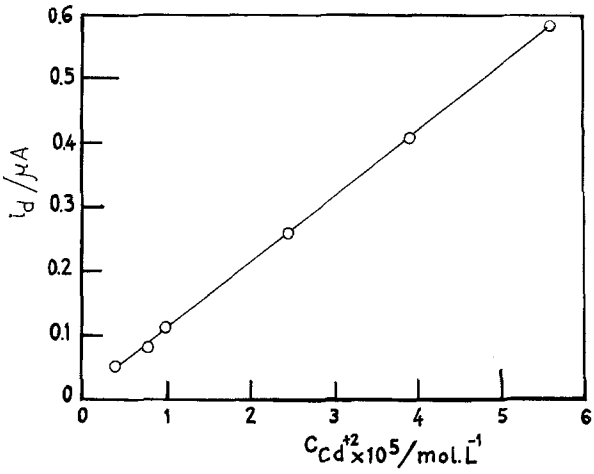

Fig. 1. Dependence of i_d on Cd^{2+} concentration at 63 °C. Supporting electrolyte 0.15 mol·L^{-1} NaCl

where n_c is the number of carbon atoms in the hydrocarbon chain and r_{ph} is the radius of the hydrated polar head. This radius was computed from the ionic conductivity of the formate ion, $\lambda_0 = 54.6\ S \cdot cm^2 \cdot mol^{-1}$ [9] and the equation:

$$r = \frac{ZeF}{6\pi\eta\lambda_0}\,, \tag{8a}$$

where F is the Faraday constant. This equation yielded $r_{ph} = 0.168$ nm, then $b = 2.46$ nm.

The concentration dependence of D_M is generally due to two factors, the first one is the effect of intermicellar interactions while the second is the possible change of the micelle size and shape with concentration.

To compute the intermicellar interactions, we used the method of Corti and Degiorgio [13], which considers a hard-core repulsion, a screened Coulomb repulsion, and a London–van der Waals attraction. This gives,

$$D_M = D_{M,O}[1 + k_D(c - CMC)]\,, \tag{8b}$$

and

$$k_D = [0.5 + 2(1+x)^2(1+4x) - \frac{15}{8}(1+x)^{-1}]\bar{v}\,, \tag{9}$$

where $x \approx k^{-1}/R_H$. k^{-1} is the Debye length and $\bar{v}$ is the partial specific volume of the micelle. In

Table 1. Diffusion coefficients, hydrodynamic radius, Debye distance, volume, length, and aggregation number for sodium hexadeconoate micelles.

Concentration ($mol \cdot L^{-1}$)	D_M ($m^2 s^{-1}$) + 10^{10}	R_H (nm)	k^{-1} (nm)	$D_{M,O}$ ($m^2 s^{-1}$) + 10^{10}	$R_{H,O}$ (nm)	V_M (nm^3)	L (nm)	n (–)
0.00169[a])	–	–	–	–	–	–	–	75.8[b])
0.013[c])	–	–	–	–	–	–	–	170
0.0182	1.85	3.12	4.78	1.31	4.41	260	11.75	326
0.0214	1.01	5.72	4.24	0.897	6.43	438	16.45	550
0.214	0.84	6.87	4.24	0.768	7.51	598	20.65	750
0.0297	0.56	10.3	3.75	0.527	11.0	1620	47.75	2043
0.0367	0.392	14.7	3.44	0.375	15.4	3045	85.0	3829
0.0502	0.040	144.3[d])	3.01	0.0395[d])	146[d])	66140[d])	1749[d])	83219[d])

[a]) CMC; [b]) estimated by the dependence of n on $n_c^{2/3}$ [c]) measured at the CMC + 0.013 $mol \cdot L^{-1}$ KBr [27]; [d]) Possible overestimations (see text)

order to compute the ionic strength and then the Debye length, the concentration of free surfactant ions was taken as the CMC, and the concentration of free Na^+ ions was estimated with:

$$[Na^+] = cmc + (c - CMC)\alpha \,, \tag{10}$$

where α is the fraction of charge per micellized polar head. This value is almost invariant for a homologous series [14]. We used $\alpha = 0.35$, as an average of literature data for sodium dodecanoate ($\alpha = 0.36$ [15], $\alpha = 0.32$ [16] and $\alpha = 0.37$ [17].).

Very large rodlike micelles entangle [18], and this phenomenon will invalidate the equations employed here. This entanglement occurs in a surfactant of similar b value, hexadecyl trimethylammonium bromide, when the hydrodynamic radius is $R_H > 19.7$ nm [19]. We conclude that, except for the largest R_H value of Table 1, sodium hexadecanoate micelles are not entangled.

At high surfactant and/or salt concentration micelles are oblate elipsoids or rodlike [20], so we used the following equation to compute the micelle length L which corresponds to the determined hydrodynamic radius [21]:

$$R_H = \frac{L}{2\sigma - 0.19 - \frac{8.24}{\sigma} + \frac{12}{\sigma^2}} \,, \tag{11}$$

where L is the length of the rodlike micelle, r its radius and $\sigma = \ln(L/r)$. We took $r = b = 2.46$ nm, obtaining the L values listed in Table 1. Except for the largest concentration, the sodium hexadecanoate rodlike micelles are stiff, because their length L is less than 100 nm, the upper limit of stiffness for rodlike micelles [19].

The volume of a rodlike micelle may be computed by the equation [22]:

$$V_{rod} = \frac{4\pi b^3}{3} + 2\pi b^2 (L - 2b) \,. \tag{12}$$

The partial molar volume of micellized sodium hexadecanoate was computed by adding to the partial molar volume of micellized sodium dodecanoate (207.3 ± 0.2 cm^3/mol) [23] four times the micellized methylene group partial molar volume (15.6 ± 0.7 cm^3/mol) [24], and the volume of 10 hydration water molecules. This hydration number was found in various micellized sodium soaps [25, 26]. The volume of a hydrated micellized surfactant molecule results in $V_s = 0.797 \pm 0.005$ nm^3, and the specific volume $\bar{v} = 0.981 \pm 0.007$ cm^3/g.

The aggregation numbers computed by $n = V_{rod.}/V_s$ are listed in Table 1.

When $\log n$ is plotted vs. $\log [X]$, $[X]$ being the concentration of counterions, different straight lines are obtained for spherical and rodlike micelles [22]. The data of Table 1 are plotted in such a manner in Fig. 2, together with one literature value of $n = 170$ for sodium hexadecanoate in 0.013 $mol \cdot L^{-1}$ NaCl [27]. The equation of the straight line, fitted by the least squares method

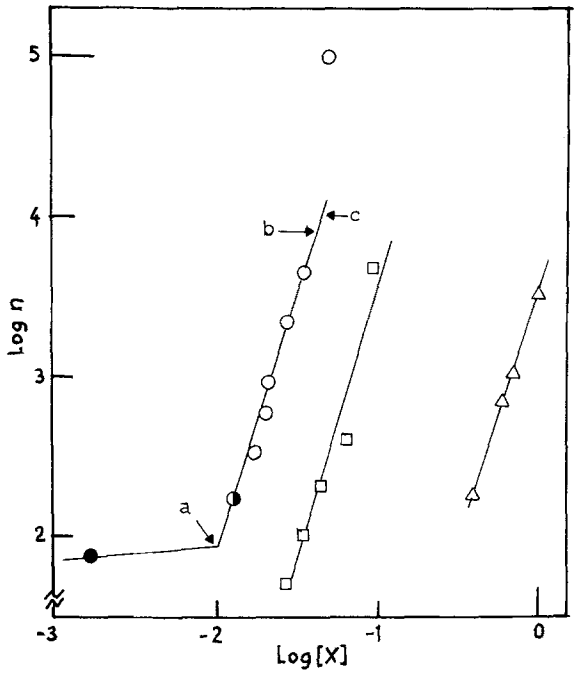

Fig. 2. Plot of Log n vs. Log $[X]$ for; □: sodium dodecanoate [17]; ▲: Potassium dodecanoate [14]; ○: Sodium hexadecanoate, ●: sodium hexadedcanoate, estimated value, ◑: sodium hexadecanoate, from reference [27]. a: maximum concentration for spherical micelles, b: upper limit for stiff rodlike micelles, c: upper limit for non-entangled rodlike micelles

(without the largest n value) is:

$$\log n = 7.899 \pm 0.060 + (3.030 \pm 0.036)\log [X] \quad (13)$$

$[X]$ in mol · L^{-1}
($r = 0.99119$ = correlation coefficient).

Spherical micelles may exist until a critical aggregation number (n_{crit}) is reached. They are given by the micelle whose radius is b [26]:

$$n_{crit} = \frac{(4/3)\pi(b - 2r_{ph})^3}{(n_c - 1)V_{CH2} + V_{CH3}}, \quad (14)$$

where V_{CH2} and V_{CH3} are the volumes of methylene and methyl groups and n_c is the number of carbon atoms in the molecule. n_{crit} is equal to 90 for sodium hexadecanoate. This corresponds to a concentration $[X] = 0.0110 \pm 0.0011$ mol · L^{-1} in Fig. 2.

When n is plotted against n_c^2, a straight line is obtained [12, 21]. By using literature [14, 17, 28] n values at the CMC for several sodium soaps, we estimated $n = 75.8$ for sodium hexadecanoate at the CMC (CMC = 0.00169 mol · L^{-1} [18]), which was also plotted in Figure 2.

The upper limit for stiff rodlike micelles is $L = 100$ nm [19], corresponding to $n = 4614 \pm 29$ and $c = 0.0401 \pm 0.0034$ mol · L^{-1}. The limit for non-entangled micelles is $R_H = 19.7$ nm, which corresponds to $L = 125$ nm, $n = 5807 \pm 36$ and $c = 0.0433 \pm 0.0036$ mol · L^{-1}. This indicates that the micelles at the highest concentration are flexible and entangled, so Eqs. (6) and (11) may not be employed. Thus, the value of n at this concentration in Table 1 must be unrealistic.

By comparison, data of rodlike micelles of other soaps were plotted in Fig. 2 giving the straight lines whose least squares equations are:

Sodium dodecanoate :

$$\text{Log}n = 7.0 \pm 1.5 + (3.4 \pm 1.2)\text{Log}\,[X] \quad (15)$$

($r = 0.93054$).

Potassium tetradecanoate:

$$\text{Log}n = 3.053 \pm 0.042 + (3.13 \pm 0.17)\text{Log}\,[X] \quad (16)$$

($r = 0.99944$).

It may be seen that the three straight lines are almost parallel to each other, giving strong support to our data.

Conclusions

Except at very dilute concentrations, below 0.011 mol · L^{-1}, sodium hexadecanoate micelles are rodlike. At concentrations over 0.040 mol · L^{-1}, the micelles are flexible, and they are entangled at concentrations over 0.043 mol · L^{-1}. Above this concentration, the polarographic measurements may give an overestimation of micelle size.

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