Physicochemical Properties of Eicosane-1,20-bis(trimethylammonium) Dibromide in Aqueous Solution

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The physicochemical properties of a cationic α,ω-type(bolaform) surfactant, eicosane-1,20-bis(trimethylammonium) dibromide ($C_{20}Me_6$), were investigated by means of surface tension, electrical conductivity, density, dye solubilization, fluorescence, and light scattering. The results obtained for $C_{20}Me_6$ were compared with those for decyltrimethylammonium bromide ($C_{10}Me_3$). The surface tension measurement suggests that $C_{20}Me_6$ has a folded, "wicket-like" conformation at the air-water interface. The cmc of $C_{20}Me_6$ was smaller than that of $C_{10}Me_3$. The apparent ionization degree of $C_{20}Me_6$ was larger, and the polarity of the micellar Stern layer was higher than that of $C_{10}Me_3$. It was found that the $C_{20}Me_6$ micelle has an aggregation number of about 19, a hydrodynamic radius of 16 Å, and a partial molar volume of 480.49×10^{-3} dm^3 mol^{-1}, suggesting that the micelle is nearly spherical; thus, the main alkyl chain is almost stretched, and the outermost region of the micelle is loose.

The α,ω-type surfactant is different from a "conventional" surfactant since the former has headgroups at each end of the long alkyl chain. This feature can impose a significant constraint on the orientation and the packing of surfactant monomers within a micelle, because both ends of each α,ω-type surfactant monomer must be located on the micellar surface.

There have been several studies of the properties of α,ω-type surfactants in aqueous solution.[1–15] Menger and Wrenn[1] reported that micelles are formed for C_mMe_6 ($m>12$), and concluded that dodecane-1,12-bis(trimethylammonium) dibromide ($C_{12}Me_6$) takes a folded, "wicket-like", conformation at an air-water interface. Johnson et al.[2] confirmed that C_mMe_6 do not form ordinary micelles for $m<10$, indicating that there is considerable bending of the $(CH_2)_m$ chains in aqueous solution and air-water interfaces from measurements of the apparent molar volumes for $m=6$ and 10. In contrast, Zana et al.[4–6,9] found no evidence of conventional micellization for $C_{12}Me_6$ from density, electrical conductivity, and emf measurements, whereas $C_{16}Me_6$ and $C_{22}Me_6$ form micelles. The chemical relaxation studies indicated that $C_{22}Me_6$ monomers diffuse rapidly among the bulk and micellar pseudophases, with a rate similar to that of the conventional surfactant, dodecyltrimethylammonium bromide ($C_{12}Me_3$). Mckenzie et al.[8] estimated the hydrodynamic radii and the ionization degree of $C_{22}Me_6$ using static and dynamic light scattering; they concluded that $C_{22}Me_6$ forms micelles which are similar to those of $C_{12}Me_3$.

On the other hand, Meguro et al.[10–13] have studied the solution properties of anionic α,ω-type surfactants, and concluded that these surfactants also form small and loose aggregates.

The conformational properties of eicosane-1,20-bis(triethylammonium) dibromide ($C_{20}Et_6$) have been investigated by NMR and time-resolved fluorecence quenching.[14–16] It has been concluded that the sufractant chains of $C_{20}Et_6$ adopt a predominantly stretched conformation in micelles. However, the physicochemical properties of α,ω-type surfactants are not fully understood. Still, it is worthwhile studying the properties in the aqueous solution of an α,ω-type surfactant from a comparison of the corresponding conventional surfactants.

In this work we focused the attention on a comparison between the physicochemical property of a cationic α,ω-type surfactant, eicosane-1,20-bis(trimethylammonium) dibromide ($C_{20}Me_6$), and that of a conventional surfactant, decyltrimethylammonium bromide ($C_{10}Me_3$), which has the same head group and an alkyl chain half as long. The comparison was carried out by measuring the surface tension, electrical conductivity, static and dynamic light scattering, steady-state fluorescence quenching, density, and probe solubilization.

Experimental

Materials. The α,ω-type surfactant, $C_{20}Me_6$, was synthesized as follows: 1,20-dibromoeicosane was prepared by the dimerization of 11-bromoundecanoic acid with Kolbe's electrolysis in methanol. A white precipitate was filtered and recrystallized from methanol. The obtained dibromide was converted to $C_{20}Me_6$ according to the procedure.[1] After removing ethanol and trimethylamine, $C_{20}Me_6$ was recrystallized four times from acetone–ethanol mixtures and dried under vacuum for 48 hours. The purity of the product was confirmed to be above 99% by isotachophoresis, elemental analysis, and ^1H NMR.

Pyrene was recrystallized four times from ethanol. Orange-OT and Yellow-OB were recrystallized four times from ethanol. Pyrene-3-carbaldehyde and benzoylacetone were used as received. *N*-Hexadecylpyridinium chloride was recrystallized three times from ethanol. Decyltrimethylammonium bromide, $C_{10}Me_3$, was recrystallized three times from acetone. The water used was purified by passing it through a purification system, Milli-Q Reagent Grade Water System, until the specific conductivity of water was below

0.1 μS cm^{-1}.

Measurements. Surface-tension measurements were carried out for various concentrations of $C_{20}Me_6$ in aqueous solutions by using a Wilhelmy-type surface tensiometer (Shimadzu St-1) at 25 °C. The establishment of equilibrium was checked by repeated measurements at 5-minute intervals. The electrical conductivity of $C_{20}Me_6$ solutions was measured by means of an electrical-conductivity meter (Toa Denpa Co. Model CM-30ET) at 25±0.1 °C.

Information about micellar aggregation numbers was obtained by static light-scattering measurements. The scattered intensities were measured at 90° using a light-scattering photometer (DLS-700 (Otsuka electronics Co.)) with an argon laser at 488 nm (13 mW). The average molecular weight of micelles was determined by using the Debye relation. The refractive index increment was measured by a differential refractometer (RM-102 (Otsuka electronics Co.)) at 488 nm. The solutions were previously filtered through a 0.2 μm disposable membrane filter.

The steady-state fluorescence quenching method of Turro and Yekta$^{17)}$ was carried out by using pyrene as a fluorescence probe and *N*-hexadecylpyridinium chloride as a quencher. In this experiment it was assumed that the probe and the quencher do not migrate from micelle to micelle within the lifetime of pyrene:$^{18)}$

$$\ln(I_0/I) = C_q/[\text{micelle}], \tag{1}$$

where C_q is the concentration of the quencher; I_0 and I are the fluorescence intensities in the absence and presence of the quencher. The micellar aggregation number is calculated from

$$N = (C - \text{cmc})/[\text{micelle}]. \tag{2}$$

Dynamic light-scattering measurements were carried out using a sub-micron particle analyzer (4700C (Malvern Co.)) with an argon laser of 488 nm, 5W (Spectra-Physics Co.). The scattering angle was varied from 40 to 140° for a sample with a concentration of 3.0×10^{-2} mol kg^{-1}, and the mean micellar diffusion coefficients for various concentrations were measured at 40°.

The density measurements were carried out by using a ANTON PAAR Model DMA 60 at 25±0.01 °C. The accuracy was $\pm10^{-5}$ g dm^{-3}. The apparent molar volume, ϕ, is given by$^{19)}$

$$\phi = \frac{M}{d} - \frac{1000(d-d_0)}{m\cdot d\cdot d_0}, \tag{3}$$

where M, m, d, and d_0 are the molar weight of the surfactant, the molality, the density of solution, and the density of water, respectively. The partial molar volume V is related to ϕ by

$$V = \phi + m\left(\frac{\partial\phi}{\partial m}\right)_{T,P,n_0}, \tag{4}$$

where T, P, and n_0 are the temperature, pressure, and mole number of water, respectively. The calculated V is plotted versus the micellized surfactant concentration. The partial molar volume of the micellar species was obtained by extrapolating the plot to the cmc. A similar approach was made for the concentration below the cmc.

The fluorescence spectra of the respective samples were measured by using a fluorescence spectrophotometer (Hitachi 650-10S). The excitation and emission slits were set at 7.5 and 1.0 nm, and the excitation wavelengths of pyrene and pyrene-3-carbaldehyde (PyCHO) were 335 and 356 nm, respectively. The emission spectra were measured in the range 360—520 nm for pyrene and 380—520 nm for PyCHO.

The ultraviolet spectra measurements were carried out using a Hitachi 220A UV spectrophotometer. The concentration of benzoylacetone (BZA) was 1.0×10^{-5} mol dm^{-3}. The absorbances from ketonic- and enolic-form of BZA were measured at 245 and 310 nm.

The procedure of solubilizing power measurements was carried out as follows: after the addition of excess amounts of water-insoluble dyes into the surfactant solution, these mixtures were shaken for 48 hours at 25±0.1 °C. Then, the solutions were centrifuged at 5000 rpm for 10 minutes, and the supernatant liquids obtained were diluted with ethanol. The optical density was measured at the maximal absorption band, and the concentrations of dyes were determined from a calibration of the absorbance versus the dye concentration.

Results and Discussion

Cmc. The cmc values of $C_{20}Me_6$ were found to be 7.5×10^{-3} mol kg^{-1} and 8.2×10^{-3} mol kg^{-1} from surface tension and electrical conductivity measurements, respectively. These cmc values were smaller than that of $C_{10}Me_3$ (6.8×10^{-2} mol dm^{-3}).$^{20)}$

Conformation of $C_{20}Me_6$ at Liquid-Air Interface. From the surface-tension values of $C_{20}Me_6$ as a function of the logarithm of the surfactant concentration, the occupying area per molecule at the air-water interface was found to be 78.9 Å^2 using Gibbs adsorption equation:

$$\Gamma = \frac{-1}{nRT}\cdot\left(\frac{\partial\gamma}{\partial\ln C}\right)_T. \tag{5}$$

The value of n was taken as 3 since $C_{20}Me_6$ is regarded as being a 2:1 electrolyte. γ is the surface tension mN m^{-1} and $(\partial\gamma/\partial\ln C)_T$ denotes the maximum slope of γ-log$C$ plots.

$$A = \frac{10^{16}}{N_A\Gamma}, \tag{6}$$

where A is the occupying area per molecule in square angstroms and N_A is Avogadro's number. The value of 78.9 Å^2 for $C_{20}Me_6$ was about twice that of the intrinstic surface area of the trimethylammonium head group (37.9 Å^2)$^{21)}$ suggesting that $C_{20}Me_6$ has a folded, "wicket-like" conformation at an air-water interface.$^{1,12)}$

Ionization Degree. Figure 1 shows the variation of the specific conductivity, κ, with the surfactant concentration. The apparent degree of micelle ionization, α_{ap}, was obtained$^{9)}$ as the ratio of the slope of these plots above and below the cmc. The α_{ap} value

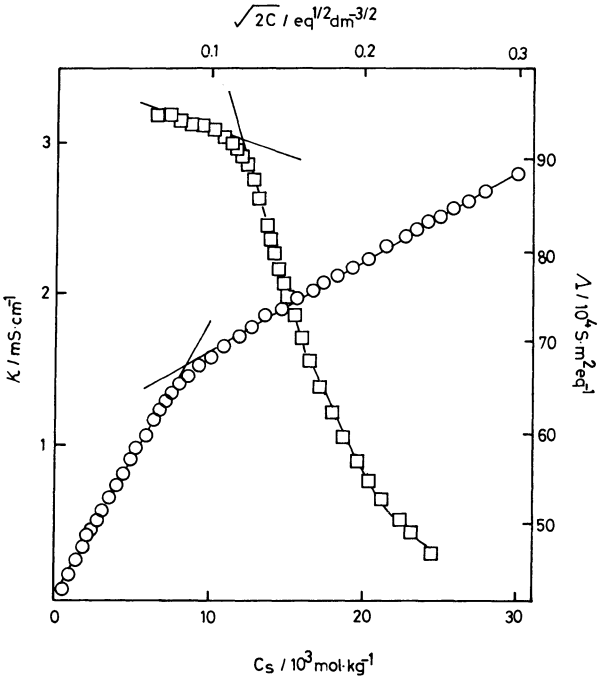

Fig. 1. Variation of specific and equivalent conductivities of $C_{20}Me_6$ with concentration in aqueous solution.

of $C_{20}Me_6$ was found to be 0.33, which is somewhat larger than that $C_{10}Me_3$. This α_{ap} value means that the minority of the fixation of the counterion is onto the micelle surface. This high value of $C_{20}Me_6$ indicates that the repulsion force between the two positive charges on trimethylammonium head for $C_{20}Me_6$ is larger than that for $C_{10}Me_3$.

Aggregation Number. From the intercept of the Debye plots at a scattering angle of 90°, the aggregation number of $C_{20}Me_6$ was found to be 18. Similarly, from a good linear relationship between $\ln(I_0/I)$ and C_q, the aggregation number of 19 was obtained by calculating the slope of this plot at the surfactant concentration 3.0×10^{-2} mol kg^{-1}. Thus, the aggregation number of $C_{20}Me_6$ obtained by static light scattering is in good agreement with that obtained by the steady-state fluorescence method. These values are nearly the half that of the aggregation number of $C_{10}Me_3$ (39—41).[22] In other words, the number of head groups per $C_{20}Me_6$ micelle is approximately the same for that of $C_{10}Me_3$ since $C_{20}Me_6$ has two head groups.

Micellar Shape. The shape of $C_{20}Me_6$ was examined by dynamic light scattering.[23,24] The initial slope, Γ, of the decay curve of the field correlation function is defined by the cumulant expansion, and the relationship between Γ and the diffusion coefficient D is generally given by

$$\frac{\Gamma}{q^2} = D_0 + \left(\frac{L^2}{12}\right)\theta f_1(q) + (D_3 - D_1)\left[f_2(q) - \frac{1}{3}\right] + \sum_m D_m a_m(q) \tag{7}$$

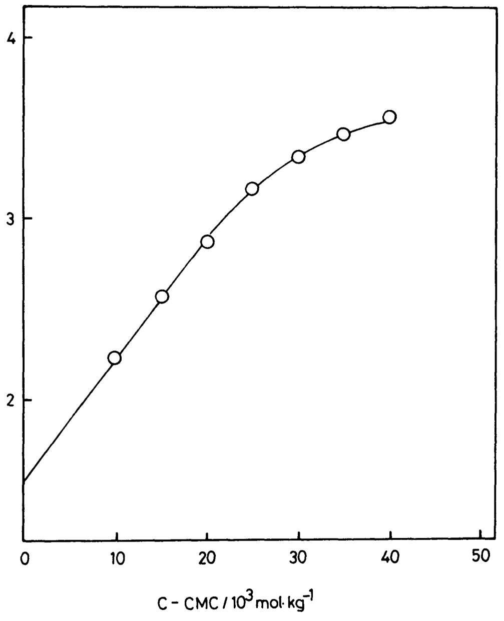

Fig. 2. Mean micellar diffusion coefficients of $C_{20}Me_6$ vs. C—cmc.

The first, second, third, and $\sum$ terms of right side of Eq. 7 are due to contributions of the average translational diffusion, the rotational diffusion, the anisotropy of the translational diffusion, and the motion of bending, respectively. Since the values of Γ/q^2 for each scattering angle are almost constant, terms including q are negligible. Accordingly, the constancy of Γ/q^2 profiles is only derived from the isotropy in the translational diffusion. Thus, this result supports the formation of the spherical micelles for $C_{20}Me_6$ in aqueous solution. The mean micellar diffusion coefficients (D) of $C_{20}Me_6$ are plotted against the surfactant concentration, i.e., C—cmc in Fig. 2. The D value increased with C—cmc due to significant net intermicellar repulsions. This behavior was analyzed according to the following equation:[25,26]

$$D = D_0(1 + KC), \tag{8}$$

where D_0 is the diffusion coefficient in limit of infinite dilution, i.e., extrapolated to the cmc. The radius of the $C_{20}Me_6$ micelle was estimated by using the D_0 value (1.55×10^{-6} cm^2 s^{-1}) and by the Stokes-Einstein equation,

$$D_0 = \frac{kT}{6\pi\eta R_H} \tag{9}$$

where k is Boltzmann's constant, T the absolute temperature, and η the viscosity of the solvent. The hydrodynamic radius value (R_H) of $C_{20}Me_6$ (16 Å) is smaller than that of $C_{10}Me_3$ calculated from reported results.[26] The D versus C—cmc plot for $C_{20}Me_6$ has a

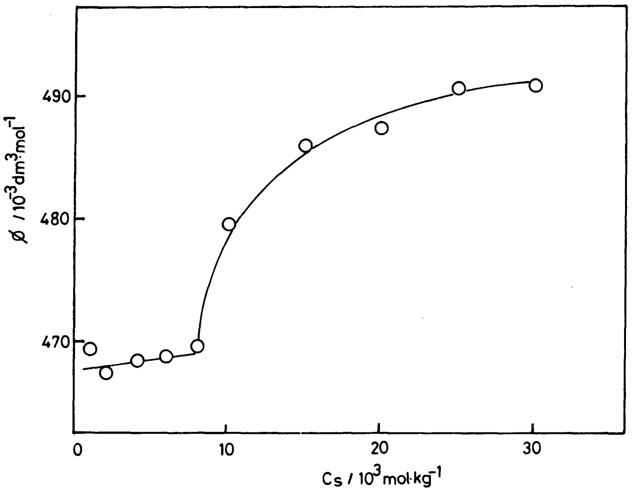

Fig. 3. Apparent molal volume of $C_{20}Me_6$ aqueous solution vs. molality of $C_{20}Me_6$.

larger slope than that for $C_{12}Me_3$.[26] This is attributed to the largeness of the ionization degree for $C_{20}Me_6$.

The partial molar volume derived from the density measurement was used to confirm the conformation of the $C_{20}Me_6$ micelle.[19] The apparent molar volumes, ϕ, are plotted against the molality in Fig. 3. This plot has a clear break, indicating the formation of the micelle of $C_{20}Me_6$. The partial molar volumes below and above the cmc were obtained with the values of 463.91 and 480.49×10^{-3} mol^{-1}, respectively.

In order to estimate the difference in micelles between α,ω-type and conventional surfactants, the surface areas occupied per head group at micelle surface(s) were calculated by some models. For this calculation, the micelle is assumed to be spherical. The superscript of "bola" means α,ω-type surfactants. Three kinds of surface areas are considered for $Br^-(C_{m''}H_{2m''+1})_3N(CH_2)_mN(C_{m''}H_{2m''+1})_3Br^-$:[21,27]

(1) s_0: s_0 is obtained by assuming a micelle radius which is equal to the length of a stretched alkyl chain, plus the length of the head group Δ, corresponding to the charged nitrogen atom and alkyl groups substituting the nitrogen atom:

$$s_0^{\mathrm{bola}} = 4\pi[(l_\mathrm{H}^{\mathrm{bola}} + 2\Delta)/2]^2/2n_0. \tag{10}$$

Here, $l_\mathrm{H}^{\mathrm{bola}}$ is only due to the methylene $(\text{-}CH_2\text{-})_m$ group,

$$l_\mathrm{H}^{\mathrm{bola}} = 1.265m,^{28,29)} \tag{11}$$

and

$$\Delta = 0.42m'' + 2.1.^{21,27)} \tag{12}$$

Equation 12 was obtained by assuming a charged nitrogen atom at the center of a regular tetrahedron having as apexes the three carbon atoms of terminal methyl groups of the three head group alkyl chains.

Table 1. Calculated and Experimental Surface Areas per Head Group

	$C_{20}Me_6$	$C_{10}Me_3$
s_o /Å^2	76.1	52.2
s_i /Å^2	37.8	37.8
s_H /Å^2	84.5	82.7
s_exp/Å^2	78.0	81.3

(2) s_i: the intrinsic surface area of the head group (s_i) is taken as being that of a circular domain having a radius equal to that of a circle determined by the same three carbon atoms of the terminal methyl groups and corrected for the void space in the packing of these circular domains in a hexagonal lattice,

$$s_\mathrm{I} = 3.46(1.205m'' + 2.1).^{2\ 21)} \tag{13}$$

(3) s_H: s_H is obtained assuming that a micelle radius is equal to the radius of a hydrophobic (oil drop-like) core, plus a length of the head group,[21]

$$s_\mathrm{H}^{\mathrm{bola}} = 4\pi(r_\mathrm{H} + \Delta)^2/2n_0. \tag{14}$$

Zana et al.[4-6] and Broadwater et al.[3] estimated the volume occupied per (CH_2) unit of bolaform alkyl chain for C_mMe_6 (m=6, 10, 16) from density measurements. The value of 15.6×10^{-3} dm^3 mol^{-1} (25.9 Å^3) per (CH_2) is adequate for a dispersed monomeric state. The volume per (CH_2) unit in the state of oil drop-like hydrocarbon should be estimated:

$$V^{\mathrm{bola}} = 26.9m.^{28,29)} \tag{15}$$

The radius of the hydrophobic core, r_H, is obtained by $r_\mathrm{H}=(3nV^{\mathrm{bola}}/4\pi)^{1/3}$ where n is the experimental aggregation number. The calculated values of s_0, s_i, and s_H, are listed in Table 1. In Table 1 the surface areas derived from the partial molar volume, s_exp, are also listed. Here, the effect of counter ions on the calculated values of s_0, s_i, and s_H is not taken into consideration. The s_exp values for both conventional and α,ω-type surfactants were fairly greater than that of s_i, indicating that the aggregations of both $C_{10}Me_3$ and $C_{20}Me_6$ are controlled by the packing of the surfactant main alkyl chain, not by the head group packing at the micelle surface. For $C_{10}Me_3$, the s_exp[30] is comparable to s_H which is derived from an assumption that the moiety of the main alkyl chain is like an oil drop. Accordingly, this result supports the idea that the hydrophobic alkyl chain of $C_{10}Me_3$ takes on an oil drop-like state in the micelle. In contrast with $C_{10}Me_3$, the s_exp value of $C_{20}Me_6$ is comparable to that of s_0 rather than s_H. Regarding s_0 it is assumed that the main alkyl chain is stretched, and has a all-trans conformation. It is thereby suggested that the state of the hydrophobic moiety of $C_{20}Me_6$ in the micelles is as follows: the aggregation behavior of

$C_{20}Me_6$ is attributed to the packing of the main alkyl chain. It is likely that the main alkyl chains of $C_{20}Me_6$ do not exist in an oil drop-like moiety, but take on an entangled, predominantly stretched conformation in the micelles.

Polarity of the Micelle. The polarity of the micelle interior was evaluated by the solubilization of two kinds of aromatic compounds, such as pyrene and pyrene-3-carbaldehyde. The intensity ratio of the first emission peak to the third one, i.e., I_1/I_3 of pyrene, is known to be sensitive to the local polarity.[31,32] This value increases upon going from nonpolar to polar solvents. Thus, pyrene can be used as an indicator of the local polarity at the solubilization site in the micelles. In low concentrations, the I_1/I_3 value was over 1.8, indicating that the pyrene monomer is located in water. At around 8.0×10^{-3} mol kg^{-1}, corresponding to the cmc, the I_1/I_3 changed down to about 1.50. This change is attributed to the solubilization of pyrene into the micelles. Since the I_1/I_3 value for $C_{10}Me_3$ is found to be 1.42 at a surfactant concentration (0.2 mol dm^{-3}), it is considered that the pyrene exists in somewhat more polar region in comparison with the conventional surfactant. Therefore, these experimental results suggest either that the interior of the $C_{20}Me_6$ micelles is polar and loose, or that the pyrene in the $C_{20}Me_6$ micelles resides at a more external site than that in the micelles of the conventional surfactant.

The fluorescence of the pyrene-3-carbaldehyde monomer strongly depends on the solvent polarity as well as pyrene.[33] The fluorescence maximum significantly shifts to the region of lower wavelength with increasing solvent polarity, showing a linear relationship with the dielectric constant for a solvent >10. Owing to the effect of the solvation in the region of the aldehyde group, PyCHO is considered to be solubilized in the micellar Stern layer.[33] The dielectric constants which denote the polarity are found to be 31.3 for $C_{20}Me_6$ and 25.4 for $C_{10}Me_3$ (Fig. 4). This result indicates that the polarity in the region of the Stern layer of $C_{20}Me_6$ micelles is higher than that of $C_{10}Me_3$

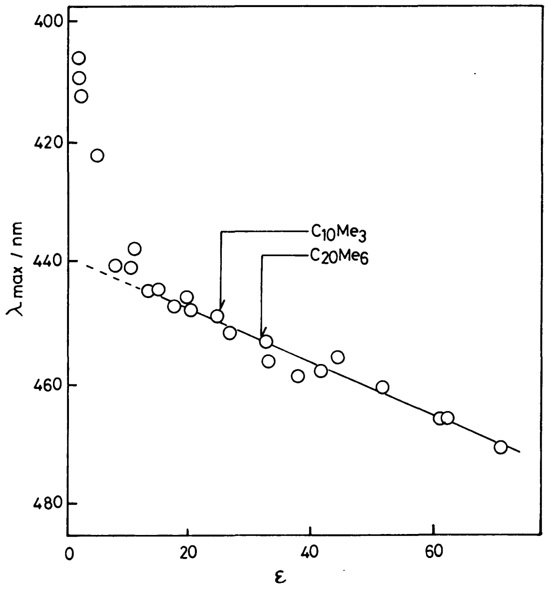

Fig. 4. Relationship between fluorescence maximum of PyCHO and solvent dielectric constant.

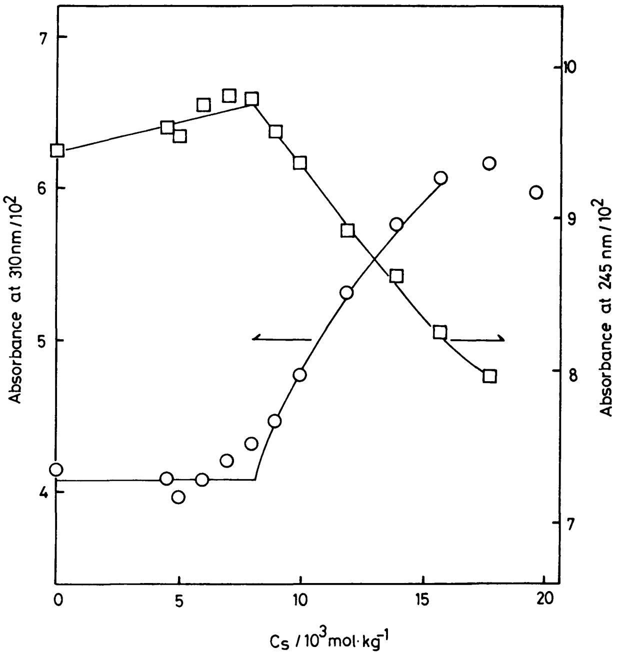

Fig. 5. Change in absorbances of BZA as a function of $C_{20}Me_6$ concentration.

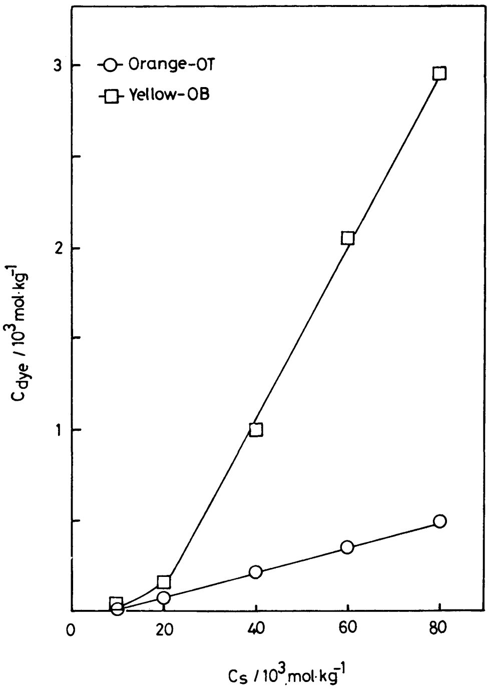

Fig. 6. Molality of Orange-OT solubilized in $C_{20}Me_6$ aqueous solution vs. $C_{20}Me_6$ concentration.

to some degree.

Solubilization of Dyes. It is known[34] that BZA exists in the enolic form in nonpolar media, whereas in the ketonic form in polar media. The change from the ketonic to the enolic form occurs when the polarity of the probe environment decreases. In Fig. 5, the absorbances of the ketonic form decrease, but the absorbances of the enolic form increase above the cmc. The distribution coefficient (α/n) between bulk and micelles is obtained by the following equation:[35]

$$\frac{1}{(C-\mathrm{cmc})}=\frac{(\varepsilon_\mathrm{m}-\varepsilon_\mathrm{w})}{(\varepsilon-\varepsilon_\mathrm{w})}\cdot(\alpha/n)-(\alpha/n), \qquad (16)$$

where ε, ε_w, and ε_m are the molar extinction coefficient in the solution, water, and micellar media, respectively. The α/n value obtained was 80, which was somewhat lower than that of $C_{12}Me_3$, dodecyltrimethylammonium bromide (α/n=90).[35]

The molality of Orange-OT solubilized in $C_{20}Me_6$ solutions versus the surfactant concentration is plotted in Fig. 6. Above the cmc, the concentrations of Orange-OT and Yellow-OB increased linearly as the surfactant concentration increased. The solubilizing power (i.e., the number of moles of the solubilized dye per mole of micellized surfactant) was obtained from the slope of the plot. The solubilizing powers were 6.9×10^{-3} and 5.6×10^{-2} moles dye per mole surfactant for Orange-OT and Yellow-OB, respectively. These values of $C_{20}Me_6$ are nearly half that of $C_{10}Me_3$. If the solubilizing power is expressed in moles of solubilized dye per mole of head group, the values of $C_{20}Me_6$ are almost one quarter of those of $C_{10}Me_3$. Further, it has been found that hydrophobic molecules are not easily solubilized into the micelles of $C_{20}Me_6$ in comparison with the corresponding conventional surfactant, $C_{10}Me_3$. Thus, the significant low capacity of the solubilizing power in $C_{20}Me_6$ micelles can be understood on the basis of the conformation of the surfactant chains. The almost stretched conformation of the alkyl chains makes it difficult for hydrophobic compounds to be incorporated into the hydrophobic core of the micelles owing to the inability for the micelles to swell.

Conclusion

The physicochemical properties of $C_{20}Me_6$ in aqueous solution have been studied by measuring the surface tension, electrical conductivity, density, dye solubilization, fluorescence, and light scattering. Further, the properties of $C_{20}Me_6$ are compared with $C_{10}Me_3$.

At the air-water interface, $C_{20}Me_6$ has a folded, "wicket-like" conformation, whereas the micelle is nearly spherical and the main alkyl chain is almost stretched. The apparent ionization degree and the polarity of the micellar Stern layer of $C_{20}Me_6$ are larger than those of $C_{10}Me_3$.

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