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New aspects of the behaviour of alkyltrimethylammonium bromide micelles : light scattering and viscosimetric studies

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Résumé. — Des solutions micellaires aqueuses de bromure de dodécyl-, tétradécyl- et hexadécyl-triméthylammonium (respectivement DTAB, TTAB et CTAB) en présence de 0,1 M KBr ont été étudiées par viscosité et diffusion de lumière élastique et quasi élastique à des concentrations allant du domaine très dilué (près de la concentration micellaire critique, CMC) au domaine semi-dilué (jusqu'à 0,42 M). Ces expériences ont montré que les micelles de DTAB sont sphériques dans tout le domaine de concentration étudié alors que les micelles de TTAB demeurent sphéroïdales jusqu'à environ 0,2 M, puis deviennent de plus en plus anisodiamétriques (probablement de forme allongée) quand la concentration augmente. Les micelles de CTAB sont déjà allongées à la CMC (le rapport des 2 axes étant de l'ordre de 6) et augmentent rapidement de taille avec la concentration en détergent. Le comportement des solutions de CTAB aux concentrations supérieures à 4×10^{-2} M, c'est-à-dire dans le domaine où les micelles allongées se recouvrent, est décrit par des lois d'échelle comme dans le cas des solutions semi-diluées de macromolécules enchevêtrées. Les exposants caractéristiques de la variation avec la fraction volumique du détergent, du coefficient de diffusion de translation et de l'intensité diffusée sont respectivement 0,75 et $-0,25$, en excellent accord avec les prédictions de la théorie des solutions semi-diluées de polymères. Cependant les résultats de viscosité montrent les limites d'applicabilité du modèle aux solutions micellaires. Des résultats obtenus précédemment pour des solutions micellaires de TTAB dans H₂O-0,1 M KBr en présence de 1-pentanol ont aussi été réanalysés.

Abstract. — Micellar solutions of dodecyl-, tetradecyl- and hexadecyl-trimethylammonium bromides (DTAB, TTAB and CTAB, respectively) have been investigated in H₂O-0.1 M KBr by means of viscosity and elastic and quasielastic light scattering, from the dilute range (near the critical micellization concentration, CMC) to the semi-dilute range (up to 0.42 M). The DTAB micelles have been shown to be spherical in the whole concentration range, whereas TTAB micelles remain spheroidal up to about 0.2 M then become increasingly anisodiametric (probably with an elongated shape) as the concentration is increased. The CTAB micelles are already prolate at the CMC (axial ratio of about 6) and grow very rapidly in size with the surfactant concentration. The behaviour of the CTAB solutions at concentration above 4×10^{-2} M, that is in the range where the prolate micelles are probably entangled, has been found to follow power laws, just like solutions of entangled polymer chains in the semi-dilute range. The exponents characterizing the change of the diffusion coefficient and of the intensity of scattered light are 0.75 and -0.25 , respectively, in excellent agreement with the prediction of the theoretical treatments for semi-dilute polymer solutions. The viscosity data however show the limits of applicability of this model to the micellar systems investigated. Previous results concerning TTAB micelles in H₂O-0.1 M KBr in the presence of 1-pentanol have been reexamined.

1. Introduction.

Elastic and quasielastic light scattering as well as viscosimetry have been extensively used in recent years to investigate the changes of micelle size and

shape, and particularly the so-called sphere-to-rod transition [1-21]. This transition from quasi-spherical to rod-like (spherocylindrical) micelles can be brought about by an increase of the concentration of the surfactant [1] or of the external electrolyte [2-4, 5-7, 16-18], by a change of micelle ionization degree [5], by additions of peculiar counterions [11-13] or alcohol

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or arenes [8], by changes of pressure [9] or temperature [2-4]. There is evidence for the existence of large elongated micelles in solutions of various surfactants such as sodium alkylsulfates [2-4, 7], tetradecylpyridinium-heptanesulfonate [13], cetylpyridinium and cetyltrimethylammonium bromides [16]. A survey of the literature reveals that the behaviour of a series of homologous surfactants in an extended range of concentration stretching from the critical micellization concentration up to 0.4-0.5 M was examined only in one study [4]. From the data reported, one would expect strong differences of behaviour in going from short to long homologs and from low to moderate concentration. We felt that such a study would be worthwhile for two reasons. First, it would give a set of results pertaining to homologous surfactants and thus would permit a distinction between the effect of surfactant chain length and concentration on the occurrence of the sphere-to-rod transition, in contrast to most of the results reported thus far which concern strongly differing surfactants. Second it would provide viscosity, scattered intensity and micelle diffusion coefficient data over an extended range of concentration. It was hoped that these data would help to clarify the behaviour of the solutions of anisodiametric micelles. Indeed, rod-like (rigid) micellar models [2-4, 10, 11], slightly flexible micellar models [12] but also worm-like (highly flexible) [6, 16-19] micellar models have been proposed to describe the behaviour of these large micelles. The recent magnetic birefringence and light scattering experiments by Appell and Porte [16-19] give strong support to a model of very flexible micelles and also evidence for some analogies between a solution of such giant one-dimensional micelles and a polymer solution [19].

This paper reports the results of an investigation of the behaviour of micelles of alkyltrimethylammonium bromides in the concentration range between the CMC and 0.42 M.

2. Materials and methods.

For the purpose of this study we have selected the dodecyl-, tetradecyl- and hexadecyltrimethylammonium bromides (DTAB, TTAB and CTAB, respectively). Indeed we have previously well characterized the behaviour of TTAB from the CMC to about 0.1 M [22, 23]. Also CTAB is known to form anisodiametric micelles upon increasing surfactant concentration [1] or added electrolyte concentration [21]. The samples of DTAB, TTAB and CTAB used in this work were the same as in previous investigations [22-24].

Elastic and quasielastic light scattering experiments were performed at 25 °C, in H₂O-0.1 M KBr in order to screen out the electrostatic repulsions between micelles, at least at low surfactant concentration, using the same apparatus as in previous

studies [22, 23]. The measurements involved the intensity and the autocorrelation function of the light scattered by the micellar solutions. Absolute values of the intensity were obtained by calibrating the apparatus by means of triply distilled and thoroughly filtered benzene. The autocorrelation of the scattered intensity was analysed by means of the cumulant method to yield the variance v of this function and the micelle diffusion coefficient D . The apparent hydrodynamic radius R_H was obtained from the Stokes-Einstein equation

$$D = kT/6 \pi \eta_0 R_H \quad (1)$$

where η_0 is the viscosity of the intermicellar solution. For spherical particles, in the limit of low volume fraction ϕ , D tends towards D_0 , the self-diffusion coefficient of the micelles and R_H is then the true hydrodynamic micellar radius. The variance v yields information on the polydispersity of micelle size and shape. In general, spherical micelles are characterized by low v -values (< 0.03), whereas anisodiametric micelles have higher v -values (up to 0.15) [2-4, 22, 23].

The viscosity measurements were performed using an Oswald viscometer [23] for viscosities lower than 50 cP and a Contraves 30 rheometer for higher viscosities.

3. Results and discussion.

The micelle diffusion coefficient, the variance v and the intensity I of the light scattered by the solution are plotted against ϕ , the volume fraction of micellized surfactant [25], in figures 1 to 3. The viscosity data plotted as $(\eta - \eta_0)/\eta_0 \phi$ (where η_0 and η are the viscosities of the solvent and solution) are shown in figure 4. Differences in behaviour in going from DTAB to TTAB and CTAB are clearly apparent. For the sake of clarity we shall first discuss the results near the CMC and then examine the variation with concentration of the properties investigated.

3.1 DILUTE RANGE. — The plots of figures 1 and 4 at low ϕ have been extrapolated to the volume fraction ϕ_{CMC} corresponding to the CMC to yield the micelle diffusion coefficient D_0 , and thus the micelle hydrodynamic radius R_H , and the value of the intrinsic viscosity $(\eta) = \lim_{\phi \rightarrow \phi_{\text{CMC}}} ((\eta - \eta_0)/\eta_0 \phi)$. Also the plot of $\phi I_s/(I - I_s)$ vs. ϕ (where I_s is the intensity scattered by the solvent) has been extrapolated to ϕ_{CMC} to yield the micelle molecular weight M which was then used to calculate the radius R of the « dry » micelle, from $R = (3 M \bar{v}/4 \pi N_A)^{1/3}$ where \bar{v} is the partial specific volume and $N_A = 6 \times 10^{23}$.

The values of R_H , R , v and (η) at the CMC are listed in table I, together with the values of the CMC's and of the length l of the surfactant molecule including its head group on the assumption of a completely

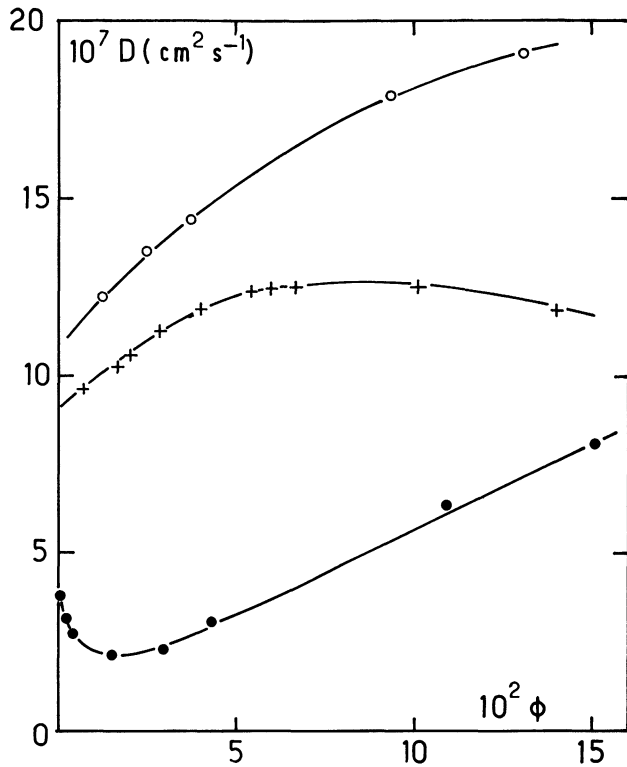


Fig. 1. — Variation of the diffusion coefficient D with the surfactant volume fraction for DTAB (O), TTAB (+) and CTAB (●).

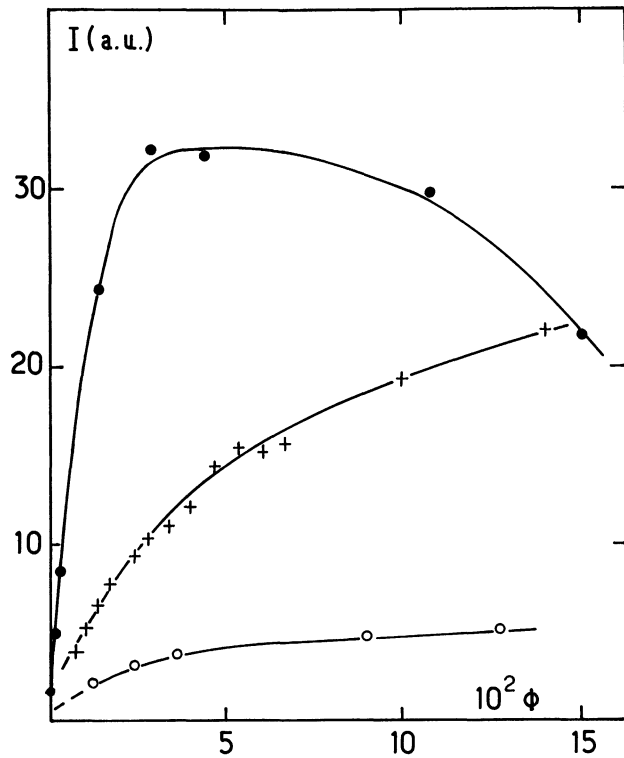


Fig. 3. — Variation of the scattered intensity I in arbitrary units with the surfactant volume fraction for DTAB (O), TTAB (+) and CTAB (●).

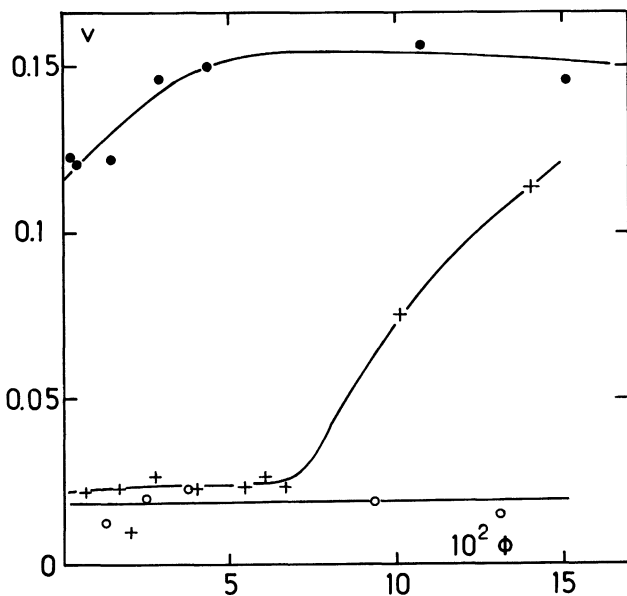


Fig. 2. — Variation of the variance v of the decay time of the autocorrelation function of the scattered intensity with the surfactant volume fraction for DTAB (O), TTAB (+) and CTAB (●).

stretched alkyl chain. For a given surfactant, l can be considered to be the radius of the minimum spherical micelle formed by this surfactant.

For DTAB, the micelle radius R is within the

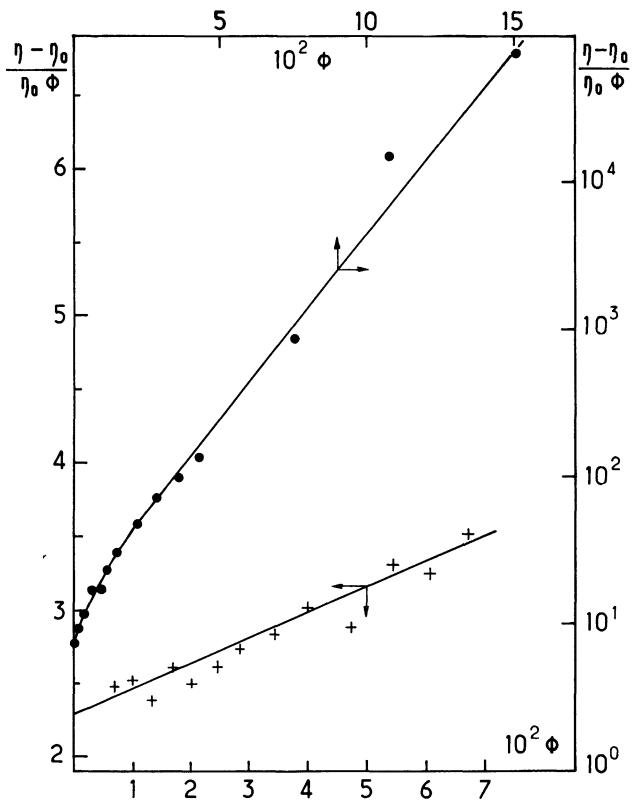


Fig. 4. — Variation of $(\eta - \eta_0)/\eta_0 \phi$ with the surfactant volume fraction for TTAB (+, 25 °C) and CTAB (●, 30 °C).

Table I. — Characteristics of the micelles of alkyltrimethylammonium bromides in H₂O-0.1 M KBr at the CMC and 25 °C.

Surfactant	CMC (^a) (M/l)	10 ⁷ D ₀ cm ² s ⁻¹	R _H (Å)	R (Å)	l (Å)	v	(η)	F(p) (^c)	F(p) (^d)	a ₁ (^e) (Å)
DTAB	1.6 × 10 ⁻³	11.2	22.25 ± 1	18.8 ± 1.5	20.2	0.01	—	—	—	—
TTAB	4.4 × 10 ⁻⁴	9.25	26.7 ± 1	25.4 ± 1.5	22.7	0.02	2.35 ± 0.3	—	—	—
CTAB	1.1 × 10 ⁻⁴	3.9 (^f)	62.4 ± 3	41.9 ± 2.5	25.3	0.12	6.5 (^b)	0.67	0.75	160

(^a) The CMC's for DTAB and CTAB have been obtained from that of TTAB, assuming a decrease of CMC by a factor 2 per additional methylene group.

(^b) Value at 30 °C.

(^c) Calculated as the ratio R/R_H (experimental values).

(^d) Calculated by inserting the *p* value in Perrin's function for prolate ellipsoids.

(^e) Calculated from the *p* value for prolate ellipsoids, taking for the semi-minor axis a length *l* = 25.3 Å.

(^f) Dorshow *et al.* [21] have measured *D*-values in 0.1 M NaBr down to 2 × 10⁻³ M. Their results generally agree with ours except for their lowest concentration point, which corresponds to a value of \bar{D} larger than in our work, where the lowest concentration investigated was 10⁻³ M. The discrepancy between the two studies may be partly due to the difference in the nature of the added salts (NaBr *versus* KBr). Nevertheless, the consistency between our light scattering and viscosity results (the latter also correspond to measurements down to 10⁻³ M) strongly support the extrapolated value of *D* found for CTAB.

experimental error equal to *l*. Also R_H is slightly larger than *R*, the difference probably represents the thickness of the micelle hydration layer [2, 22]. Indeed the micelle diffusion coefficient gives a measure of the hydrodynamic radius of the micelle, that is the micelle plus the layer of water molecules which move with the micelles in the course of their Brownian jumps. Finally the variance *v* is very small. All these results strongly suggest that DTAB micelles are spherical at the CMC.

TTAB shows a behaviour very similar to DTAB. However contrary to DTAB the difference between the values of *R* and *l* for TTAB is larger than the experimental error although still fairly small. Since *l* represents the radius of the minimum spherical micelle, the TTAB micelles at the CMC must be nearly spherical. Their quasi-spherical shape is also suggested by the value of the intrinsic viscosity (η), which is equal to that for spherical particles (2.5), within experimental error.

Contrary to DTAB and TTAB, all the results for CTAB micelles indicate that these micelles are not spherical, in agreement with the results of Dorshow *et al.* [21]. The latter clearly show that whereas the *D* vs. concentration curves for TTAB at various NaBr contents extrapolate to about the same value at the CMC, the curves for CTAB show a marked change of variation between 0.04 and 0.075 M NaBr. At above 0.075 M added NaBr, as is the case in the present work, the extrapolated value of *D* is clearly smaller than at lower salt contents, indicating micelles larger than the nearly spherical micelles found at low NaBr content. Our results listed in table I show that R_H is much larger than *R* and that both *R* and R_H are much larger than *l*. Also the variance *v* is high. Finally the value of (η) is much larger than that expected for spherical particles. The results in table I

can be used to show that the CTAB micelles are elongated. For this purpose we assume the micelles to be oblate or prolate ellipsoids with a semi-minor axis equal to *l* = 25.3 Å, the length of the surfactant ion. Perrin [26] has given the expression for the diffusion coefficient of such particles as a function of *l* and *p*, the ratio of the semi-major to the semi-minor axis of the ellipsoids. Inserting the values of *D*₀ and *l* and solving these expressions for *p* one obtains

$$p = 3.2 \quad \text{for oblate ellipsoids}$$

and

$$p = 6.3 \quad \text{for prolate ellipsoids.}$$

On the other hand, if R_s is the radius of the spherical micelle having the same volume as the ellipsoid of hydrodynamic radius R_H one can write

$$R_s = R_H F(p)$$

where *F*(*p*) is Perrin's function. To a first approximation, neglecting hydration effects, R_s can be set equal to *R*, the micelle radius obtained from the scattered intensity *I*. Indeed *I* is very insensitive to the particle shape up to *p* values of 50 but depends on the particle volume. Thus it is found that *F*(*p*)=0.67. This value is to be compared with those obtained by inserting the above *p* values into the expressions of *F*(*p*) for oblate and prolate ellipsoids, 0.89 and 0.75, respectively. Thus a much better agreement is found when assuming a prolate shape. The (η) value found for CTAB micelles leads to the same conclusion. Indeed the intrinsic viscosity of a solution of compact ellipsoidal particles is given by [27],

$$(\eta) = A(p)$$

where *A*(*p*) is a function of *p* tabulated for oblate and prolate ellipsoids. From the experimental value

of (η) we found $p = 8$ and 6 assuming oblate and prolate shapes, respectively. Thus the p values from viscosity and quasielastic light scattering are in very good agreement for the prolate shape and disagree for the oblate shape. Note that in the calculation of $F(p)$ from R and R_H we have neglected the fact that the thickness of the hydration layer is included in the value of R_H but not in that of R . If R were increased by 2 \AA , the approximate thickness of the hydration layer (see above), the agreement between the two values of $F(p)$ would be even better for the prolate shape (0.70 vs. 0.75). Also a model of spherocylindrical micelles is probably more realistic than a model which assumes prolate ellipsoid micelles. This however should not affect the conclusion reached above, namely that the CTAB micelles at the CMC in H_2O - 0.1 M KBr are elongated with an axial ratio of about 6 [28].

3.2 EFFECT OF CONCENTRATION. — For DTAB, the variance v remains constant and small (< 0.02), the diffusion coefficient increases almost linearly and $\phi I_s/(I - I_s)$ increases linearly, when ϕ is increased up to 0.13 which corresponds to a concentration of 0.42 M . A similar behaviour is seen for TTAB up to 0.2 M . All these results suggest that DTAB and TTAB micelles remain spherical or close to spherical in these concentration ranges. The changes of D and $\phi I_s/(I - I_s)$ simply reflect the increase of intermicellar interactions and the results permit the evaluation of the interaction parameters k'_I and k'_F , for the osmotic compressibility and the friction coefficient from [29]:

$$\frac{\phi}{I - I_s} = \left(\frac{\phi}{I - I_s} \right)_{\phi \rightarrow 0} (1 + k'_I \phi)$$

$$D = D_0 \frac{1 + k'_I \phi}{1 + k'_F \phi}$$

For this purpose we first determined k'_I from the scattered intensity data, then k'_F was obtained by plotting $D_0(1 + k'_I \phi)/D = 1 + k'_F \phi$ against ϕ . The plots are linear except for a deviation in the higher concentration range in the case of TTAB, as can be seen on figure 5. The values of k'_I and k'_F are listed in table II, together with the corresponding data for SDS from the work of Corti and Degiorgio [29]. Both k'_I and k'_F increase in the sequence $\text{SDS} > \text{DTAB} > \text{TTAB}$. This is the same sequence as the micelle ionization degrees. Such a result was to be expected since the intermicellar electrostatic repulsions are the predominant factor in determining the magnitude of the interaction parameters [29].

For TTAB the variance v increases rapidly with ϕ , at $\phi > 0.07$. Also D goes through a maximum at about the same volume fraction, and then decreases. Finally, at high ϕ , the $\phi I_s/(I - I_s)$ vs. ϕ plot shows an upward curvature and the quantity $D_0(1 + k'_I \phi)/D$ deviates from linearity. All these results suggest a change of shape of the TTAB micelles at high ϕ . Most likely, in

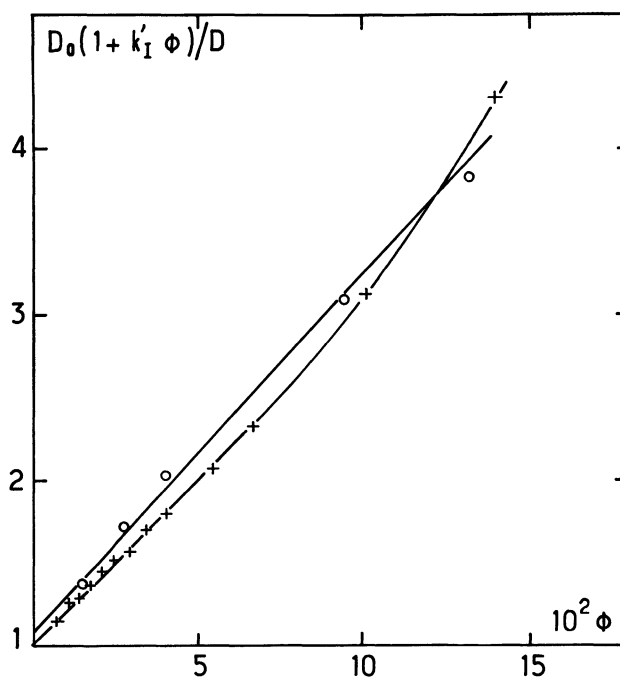


Fig. 5. — Variation of $D_0(1 + k'_I \phi)/D$ with the surfactant volume fraction for DTAB (O) and TTAB (+).

Table II. — Interaction parameters.

	SDS	DTAB	TTAB
k'_I	47.1	42.4	32.8
k'_F	28.2	20.3	18.8

view of the results for the longer homolog CTAB, these micelles grow and become elongated. In that respect, the behaviour of TTAB micelles appears as intermediate between that of DTAB micelles which remain spherical from the CMC to 0.42 M , and of CTAB micelles which are elongated in the same concentration range, as indicated by the large value of v .

The behaviour of CTAB micelles, however, is rather complex, as shown by the concentration dependence of D . Indeed D first exhibits a sharp decrease and then goes through a minimum at $\phi \sim 0.015$ (that is $C \sim 0.04 \text{ M}$). A very similar behaviour has been reported by Dorshow *et al.* [20, 21] for micellar CTAB solutions in the presence of NaBr. However, these experiments did not extend to surfactant concentrations as high as in the present work and thus did not allow the observation of the large increase of D at high ϕ which can be seen on figure 1. Nevertheless these authors attributed the initial decrease of D to micellar growth, contrary to the analysis of Corti and Degiorgio [29] who explained this effect (observed also with SDS micelles at high NaCl concentration) on the basis of intermicellar interactions which become attractive at sufficiently high ionic strength. In the present work we have obtained direct evidence for micelle growth

at low ϕ from the measurement of the micelle aggregation number N_a by means of the fluorescence probing method [30] previously used to investigate the aggregation behaviour of surfactants. The measurements performed at 30°, owing to experimental constraints, yielded $N_a = 430 \pm 50$ at $\phi = 5.4 \times 10^{-3}$ ($C = 1.485 \times 10^{-2}$ M) whereas at $\phi \geq 1.2 \times 10^{-2}$ ($C \geq 3 \times 10^{-2}$ M) the aggregation number was so large that the method was no longer capable of yielding a meaningful value of N_a . At high surfactant concentration these large micelles, which are probably flexible [6, 16-19] should overlap forming a transient network similar to an entangled polymer solution. In the following, this similarity will be used as a basis for the interpretation of the behaviour of concentrated CTAB micellar solutions.

Thus, as for polymer solutions, the cross-over volume fraction from the dilute solution of anisodiametric micelles to the semi-dilute solution of entangled micelles, which form a micellar network, should correspond to the ϕ -range where the average micelle size, characterized by its radius of gyration, becomes comparable to the mean distance between the centres of the particles. As for polymer solutions, this volume fraction will be referred to as ϕ^* . The relevant parameter for these systems at $\phi > \phi^*$ is the so-called « screening length » ξ . Thus in the theoretical work of De Gennes [31] and Des Cloizeaux [32] (based on the analogy between ferromagnets and polymer solutions) it was shown that in the semi-dilute range, for polymer solutions in good solvents, ξ obeys the following scaling law

$$\xi \sim \phi^{-3/4}$$

and is independent of the number N of statistical units of the chain. This relationship means that the semi-dilute polymer solution can be simply visualized as a polymer net with a mesh size ξ which decreases rapidly as ϕ is increased. The light scattered from such systems arises mainly from a collective excitation of the network, and its intensity I_{SD} is predicted to vary with ϕ according to

$$I_{SD} \sim \phi^2 \xi^{-3} \sim \phi^{-0.25}.$$

The quasi-elastic light scattering provides a measurement of the cooperative diffusion constant D_c associated with the collective modes of many chains. This coefficient is inversely proportional to ξ , thus

$$D_c \sim \xi^{-1} \sim \phi^{0.75}.$$

Semi-dilute polymer solutions have been found to obey the above scaling laws as a function of ϕ , independently of N . However the exponent of the power law of D_c was found to be lower than 0.75, generally of about 0.67. This difference was attributed to the fact that dynamical properties converge much more slowly than static properties, to the asymptotic limit ($N \rightarrow \infty$), where scaling theories apply [33, 34].

The examination of figures 1 and 3 shows that the behaviour of micellar CTAB solutions is well described

by the polymer chain model. Above a concentration of about 0.05 M (that is $\phi \sim 0.019$), which would correspond to the cross-over volume fraction ϕ^* , the scattered intensity decreases and the diffusion coefficient increases upon increasing ϕ . Figure 6 shows that the plots of $\log D$ and $\log I$ vs. $\log \phi$ are linear at $\phi > \phi^*$, and yield exponents equal to -0.25 and 0.75 . The agreement between these values and the predicted ones is excellent in view of the complexity of the system investigated and the assumption that it behaves like polymer solutions in the semi-dilute range.

The viscosity results have also been examined on this assumption. The reptation theory, developed by Edwards [35] for solutions of entangled polymer chains, predicts a scaling dependence of the relative viscosity $\eta_r = (\eta - \eta_0)/\eta_0$, as a function of both the polymer concentration and number of statistical units per chain, according to

$$\eta_r \sim \phi^{3.75} N^3.$$

For the CTAB solutions, the results in figure 4 yielded a $\log \eta_r$ vs. $\log \phi$ plot showing an asymptotic behaviour with a slope close to 8, that is much larger than predicted. The difference may be partly due to an increase of N with ϕ (indeed, the fluorescence data described above suggest an increase of micelle size, which may be accompanied by an increase of N). Also, at such high ϕ , the ionic strength 0.1 M KBr may no longer be sufficient to achieve a complete screening of the intermicellar repulsions. Then the contribution of the electroviscous effect to the viscosity of the system is expected to increase rapidly with ϕ , resulting in the observed behaviour.

Thus, the viscosity results clearly show the limits of the similarity between entangled polymer solutions and concentrated micellar CTAB solutions. Nevertheless, this model gives a consistent description of the elastic and quasi-elastic light scattering by these solutions. The validity of such a model should extend to other surfactant systems where very elongated micelles can be formed in various conditions as in CTAB solutions. This prediction can be to a certain extent checked with our previous light scattering and viscosity results [23] which suggested that the addition of pentanol to TTAB micelles in H₂O-0.1 M KBr induced a growth of the micelles. For pentanol contents above 0.08 M, the dependences of D and I on ϕ were very similar to those for CTAB. The $\log D$ and $\log I$ vs. $\log \phi$ plots are linear (see Fig. 6) indicating that these systems obey power laws, just like CTAB. However the exponents are about 0.67 for D and -0.24 for I , that is comparable to those found for polymer solutions but smaller than for CTAB as far as D is concerned. Also the viscosity data yielded exponents lower than 3.75, that is much smaller than for CTAB. The main reason for the differences between the CTAB and TTAB-pentanol systems is that whereas the micelle size increases very rapidly with ϕ for the former, an opposite behaviour was found for the latter [36].

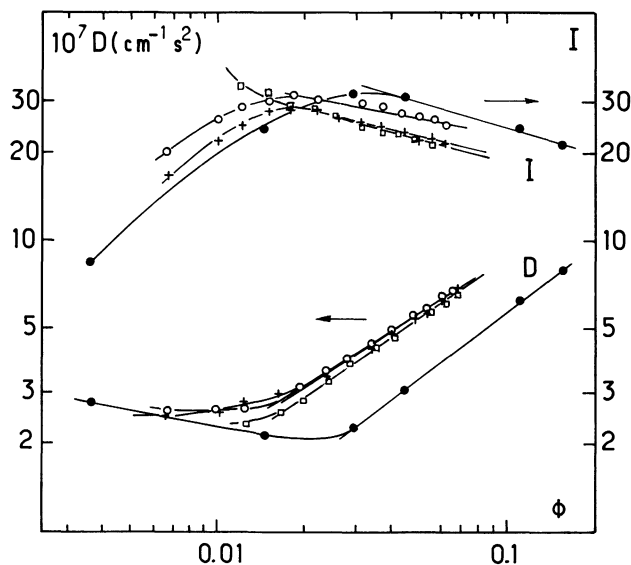


Fig. 6. — Plots of $\log D$ and $\log I$ against $\log \phi$ for CTAB in H_2O -0.1 M KBr (●) and for TTAB in H_2O -0.11 M pentanol, 0.1 M KBr (○), in H_2O -0.148 M pentanol, 0.1 M KBr (+) and in H_2O -0.1865 M pentanol, 0.1 M KBr (□).

4. Conclusions.

The data reported above indicate that at the CMC in H_2O -0.1 M KBr the DTAB and TTAB micelles are spherical whereas CTAB micelles are elongated (axial ratio ~ 6). As the surfactant concentration is increased, the DTAB micelles remain spherical up to 0.42 M, while the TTAB micelles remain spheroidal only up

to about 0.2 M, then probably become elongated. Finally the CTAB micelles grow more and more in size. At high concentration the behaviour of micellar CTAB solutions can be described by the theoretical treatments presented for solutions of entangled polymer chains (semi-dilute range). The exponents obtained for the scattered intensity and diffusion coefficient are in excellent agreement with the theoretical predictions. This agreement may be partly fortuitous and clearly additional experiments on systems where elongated micelles are known to be formed appear necessary. Nevertheless it is felt that the above results give strong evidence for the flexibility of the elongated giant micelles, which has been a subject of controversy in the recent years. Such a high flexibility may appear surprising at first sight, in view of the large cross-section of these elongated micelles (about 55 Å for CTAB) compared with their total length (a few hundred Å). It must be recalled however that the surfactant molecules retain a very high lateral mobility in the micelles [37]. This added to the high conformational mobility of the surfactant alkyl chain makes it possible for the chain packing to readjust very rapidly when a fold occurs in an initially linear part of such elongated micelle. Finally it must be noted that the evidence for a cylindrical polymer-like phase in the phase diagram of microemulsions has also been recently predicted [38].

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References

- [1] REISS-HUSSON, F. and LUZZATTI, V., *J. Phys. Chem.* **68** (1964) 3504.
- [2] MAZER, N., BENEDEK, G. and CAREY, M. C., *J. Phys. Chem.* **80** (1976) 1075.
- [3] YOUNG, C., MISSEL, P., MAZER, N., BENEDEK, G. and CAREY, M., *J. Phys. Chem.* **82** (1978) 1375.
- [4] MISSEL, P., MAZER, N., BENEDEK, G. and CAREY, M., *J. Phys. Chem.* **87** (1983) 1264.
- [5] IKEDA, S., TSUNODA, M. A. and MAEDA, H., *J. Colloid Interface Sci.* **70** (1979) 448.
- [6] IKEDA, S., OZEKI, S. and TSUNODA, M. A., *J. Colloid Interface Sci.* **73** (1980) 27; OZEKI, S. and IKEDA, S., *ibid.* **77** (1980) 219.
- [7] HAYASHI, S. and IKEDA, S., *J. Phys. Chem.* **84** (1980) 744; IKEDA, S., HAYASHI, S. and IMAE, T., *J. Phys. Chem.* **85** (1981) 106.
- [8] ULMUS, J., LINDMAN, B., LINDBLUM, G. and DRAGENBERG, T., *J. Colloid Interface Sci.* **65** (1978) 88.
- [9] NICOLI, D., DAWSON, D. and OFFEN, H., *Chem. Phys. Lett.* **66** (1979) 291.
- [10] SCHORR, W. and HOFFMANN, H., *J. Phys. Chem.* **85** (1981) 3160.
- [11] HOFFMANN, H., PLATZ, G. and ULBRICHT, W., *J. Phys. Chem.* **85** (1981) 3160.
- [12] (a) HOFFMANN, H., PLATZ, G., REHAGE, H. and SCHORR, W., *Ber. Bunsenges Phys. Chem.* **25** (1981) 877; (b) *Adv. Colloid Interface Sci.* **17** (1982) 275.
- [13] HOFFMANN, H., REHAGE, H., PLATZ, G., SCHORR, W., THURN, H. and ULBRICHT, W., *Colloid Polym. Sci.* **260** (1982) 1042.
- [14] NAGARAJAN, R., SHAH, K. and HAMMOND, S., *Colloid Surf.* **4** (1982) 147.
- [15] NAGARAJAN, R., *J. Colloid Interface Sci.* **90** (1983) 477.
- [16] PORTE, G., APPELL, J. and POGGI, Y., *J. Phys. Chem.* **84** (1980) 3105.
- [17] PORTE, G. and APPELL, J., *J. Phys. Chem.* **85** (1981) 2511.
- [18] APPELL, J., PORTE, G. and POGGI, Y., *J. Colloid Interface Sci.* **87** (1982) 492.
- [19] APPELL, J. and PORTE, G., *J. Phys. Lett.* **44** (1983) L-689.
- [20] DORSHOW, R., BRIGGS, J., BUNTON, C. and NICOLI, D., *J. Phys. Chem.* **86** (1982) 2388.

- [21] DORSHOW, R., BUNTON, C. and NICOLI, D., *J. Phys. Chem.* **87** (1983) 1409.
- [22] CANDAU, S. and ZANA, R., *J. Colloid Interface Sci.* **84** (1981) 206.
- [23] HIRSCH, E., CANDAU, S. and ZANA, R., *J. Colloid Interface Sci.* **88** (1982) 428 and *ibid.* **97** (1984) 318.
- [24] ZANA, R., *J. Colloid Interface Sci.* **78** (1980) 330.
- [25] The volume fraction ϕ of the surfactant was taken as $10^{-3} C\bar{V}$ where C is the molar concentration and \bar{V} the partial molal volume in the micellized state. The value of \bar{V} is known for TTAB [23]. Those for CTAB and DTAB were obtained by adding and subtracting $34 \text{ cm}^3/\text{mole}$ to this value. Indeed the partial molal volume increment per mole of micellized CH_2 is about $17 \text{ cm}^3/\text{mole}$ (Corkill, J. M., Goodman, J. and Walker, T., *Trans. Faraday Soc.* **63** (1967) 768).
- [26] PERRIN, J., *J. Physique* **5** (1934) 498 ; **6** (1936) 1.
- [27] DAUNE, M., FREUND, L. and SPACH, G., *J. Chem. Phys.* **59** (1962) 485.
- [28] The axial ratio p is found equal to 6.7 from the light scattering data if a spherocylindrical like micelle is used with a radius of both cylinder and half-spheres equal to 25.3 \AA . The length of the cylinder is then 120 \AA .
- [29] CORTI, M. and DEGIORGIO, V., *J. Phys. Chem.* **85** (1981) 711.
- [30] LIANOS, P. and ZANA, R., *J. Colloid Interface Sci.* **84** (1981) 100.
- [31] DE GENNES, P. G., *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca (N.Y.)) 1979.
- [32] DES CLOIZEAUX, J., *J. Physique* **36** (1975) 281.
- [33] WEILL, G. and DES CLOIZEAUX, J., *J. Physique* **40** (1979) 99.
- [34] AKCASU, A. and HAN, C. C., *Macromolecules* **12** (1979) 276.
- [35] EDWARDS, S. F., *Proc. Phys. Soc.* **92** (1967) 9.
- [36] As part of this work we found by means of fluorescence probing (24) that the micelle aggregation of TTAB in H_2O - 0.1 M KBr- 0.05 M pentanol decreased from 410 to 270 and 225 as the surfactant concentration was increased from $2 \times 10^{-2} \text{ M}$ to $4 \times 10^{-2} \text{ M}$ and $6 \times 10^{-2} \text{ M}$.
- [37] TABONY, J., LLOR, A. and DRIFFORD, M., *Colloid Polym. Sci.* **261** (1983) 938.
- [38] SAFRAN, S. A., TURKEVICH, L. A. and PINCUS, P., *J. Physique Lett.* **45** (1984) L-69.
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