

Are Large Micelles Rigid or Flexible? A Reinterpretation of Viscosity Data for Micellar Solutions

R. NAGARAJAN

Department of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

Received January 20, 1982; accepted February 24, 1982

Surfactant solutions in which large cylindrical micelles form are characterized by two essential features, namely, they are polydisperse and the average micelle size is proportional to the square root of the micelle concentration. These features of the cylindrical micelles imply that the intrinsic viscosities of these micellar solutions should also depend on the concentration of micelles. This fact has been ignored in all past treatments of micellar viscosity data. Here, viscosity data available in literature were reexamined in terms of concentration-dependent intrinsic viscosity so as to evaluate the rigidity or the flexibility of the large micelles. It is found that the interpretation of viscosity data assuming that the large micelles are rigid rods is in very good agreement with the theoretically anticipated essential features of large micelles. It is concluded that large micelles can be satisfactorily represented by rigid rods rather than by flexible rods or coils.

INTRODUCTION

Surface-active molecules self-assemble in aqueous solutions to form small spherical or globular micelles as well as large cylindrical micelles. The transition from the spherical to the cylindrical micelles is favored by factors which contribute to an increase in the attractive component or a decrease in the repulsive component of the free energy of micellization (1-3). For conditions under which cylindrical micelles form, theoretical analysis by Mukerjee (4) has shown that the micellar solution is polydisperse and that the average micellar size increases in proportion to the square root of the concentration of micelles in solution. Mukerjee has analyzed the experimental data of Debye and Anacker (5) for hexadecyltrimethylammonium bromide, of Elworthy and McFarlane (6) for hexadecylheptoxyethylene glycol monoether, and of Balmbra *et al.* (7) for tetradecylhexoxyethylene glycol monoether, to confirm the validity of the above features of cylindrical micelles. Similar conclusions were reached in the more recent studies of Tausk

and Overbeek (8, 9) on short-chain synthetic analogs of lecithin molecules, in the theoretical analysis of micellization presented by Israelachvili *et al.* (10), and from the light-scattering studies of Mazer *et al.* (11, 12) on sodium dodecyl sulfate. Therefore, the interpretation of any experimental data for cylindrical micellar solutions should be consistent with their two essential features, namely, micellar polydispersity and the dependence of the average micellar size on the square root of the concentration of micelles in solution.

Viscometric technique has been used in a number of experimental investigations (13-17) of micellar solutions both because of its simplicity and its sensitivity to detect changes in the size of the anisotropic micellar cylinders. In the interpretation of viscometric data, all studies usually assume, for simplicity, a monodispersion of micelles. The intrinsic viscosity $[\eta]$ of the micellar solution is then determined by extrapolating the experimental data of (specific viscosity/concentration of micelles) vs concentration of micelles to the critical micelle concentration (CMC). This intrinsic viscosity data in con-

junction with micellar molecular weights estimated from light-scattering measurements have been used to conclude that cylindrical micelles are not rigid but likely to be flexible (16, 18). To describe such flexible micelles, an intuitively appealing physical model has been suggested by Stigter (18).

The main goal of this paper is to emphasize that the intrinsic viscosity of cylindrical micellar solutions should be dependent on the surfactant concentration because the size of the micelle depends significantly on the surfactant concentration. This is in marked contrast to nonassociating macromolecular solutions where the intrinsic viscosity representative of macromolecular size is defined to be concentration independent. Therefore, the intrinsic viscosities of micellar solutions reported in literature which fail to account for its concentration dependence are not satisfactory in representing the sizes of the large cylindrical micelles. This also implies that the conclusions based on such data as to the flexibility of large micelles need to be reexamined.

In this paper, we recalculate the intrinsic viscosities of micellar solutions using the well-known viscometric data of Kushner *et al.* (13) for dodecylammonium chloride, and the more recent viscometric data of Ozeki and Ikeda (16) for dodecyldimethylammonium chloride and of Hoffman *et al.* (17) for dodecylammoniumtrifluoroacetate. The intrinsic viscosities are computed assuming that micelles are monodispersed, because we have shown earlier (19) that the viscosity calculated assuming polydispersity is quite close to that calculated assuming monodispersity. The present calculations show that for many of the surfactant systems mentioned above, the interpretation of viscosity data assuming that micelles are rigid rods agree very well with the theoretical dependence of the micellar size on the square root of the micellar concentration. This automatically implies that the micellar solution is polydisperse, as is required by theory (4). For systems where disagreement exists between the viscometric

data and the theoretically anticipated behavior, plausible causes for the discrepancy including the flexibility of micelles are investigated. We conclude that the large micelles are represented more accurately by rigid rods rather than by flexible coils.

THERMODYNAMICS AND HYDRODYNAMICS OF LARGE MICELLES

For dilute surfactant solutions in which the intermicellar interactions are not important, the micelle size distribution is given by (1, 20, 21)

$$X_g = X_1^g \exp[-g(\mu_g^0 - \mu_1^0)/kT], \quad [1]$$

where X_g is the mole fraction of micelles of size g , X_1 is the mole fraction of the singly dispersed amphiphiles, μ_g^0 is the standard chemical potential per surfactant molecule incorporated into the micelle, μ_1^0 is the standard chemical potential of the surfactant in water, k is the Boltzmann constant and T is the absolute temperature. When the standard chemical potentials are such as to favor cylindrical micelles and when the total surfactant concentration X ($X = \sum_{g=1}^{\infty} gX_g$) is large compared to that of the singly dispersed amphiphile X_1 , the size distribution equation has been simplified to (11)

$$X_g = (1/K) \exp[-g/\{K(X - X_{CMC})\}^{1/2}], \quad [2]$$

$g > g_s,$

where

$$K = \exp\{-g_s(\mu_c^0 - \mu_1^0)/kT\} / \exp\{-g_s(\mu_s^0 - \mu_1^0)/kT\}, \quad [3]$$

and

$$X_{CMC} = \exp\{-(\mu_c^0 - \mu_1^0)/kT\}. \quad [4]$$

In Eqs. [2] to [4], g_s is the aggregation number of the largest spherical micelle beyond which the addition of further amphiphiles gives rise to cylindrical micelles and μ_s^0 and μ_c^0 are the standard chemical potentials of a surfactant molecule present in the largest spherical mi-

celle and in the large cylindrical micelle, respectively. The parameter K represents the relative preference for the cylindrical micelles compared to the spherical micelles. Corresponding to the size distribution of cylindrical micelles represented in Eq. [2], the concentration dependence of the weight and the number average aggregation numbers of the micelles are

$$\bar{g}_w = g_s + 2[K(X - X_{CMC})]^{1/2}, \quad [5]$$

and

$$\bar{g}_n = g_s + [K(X - X_{CMC})]^{1/2}. \quad [6]$$

Equations [5] and [6] show that the theoretically predicted polydispersity index \bar{g}_w/\bar{g}_n is large and close to 2. The equivalence of various thermodynamic models (4, 8–12) for large micelles is clarified briefly in the Appendix.

For a cylindrical micelle of aggregation number \bar{g}_w , the axial ratio L/d is

$$(L/d) = \left\{ \left[\bar{g}_w v_0 - \frac{4}{3} \pi l_0^3 \right] / \pi l_0^2 \right\} + 2(l_0 + \delta) / (2[l_0 + \delta]). \quad [7]$$

In equation [7], v_0 and l_0 are the volume and the length, respectively, of the hydrocarbon tail of the amphiphile and δ is the effective length of the polar head group including adsorbed counterions and water of hydration. Here the cylindrical micelle is assumed to have hemispherical ends and the length L includes the contribution of these ends as well. Since for the largest spherical micelle

$$g_s v_0 = (4/3) \pi l_0^3, \quad [8]$$

the expression for the axial ratio (L/d) of the cylindrical micelle can be rewritten as

$$(L/d) = 1 + (2/3)[l_0/(l_0 + \delta)] \times [(\bar{g}_w/g_s) - 1]. \quad [9]$$

For the purpose of hydrodynamic calculations, a cylindrical rod of axial ratio (L/d) can be equated to a prolate ellipsoid of equal length and volume (22). The axial ratio J of such an equivalent prolate ellipsoid is

$$J = (L/d)[2/\{3 - (d/L)\}]^{1/2}. \quad [10]$$

The shape factor ν defined to account for the influence of solute size on the solution viscosity is related (22–24) to the axial ratio of the prolate ellipsoid as

$$\nu = 2.5 + 0.407(J - 1)^{1.508}, \quad 1 < J < 15, \quad [11]$$

and

$$\nu = 1.6 + \frac{J^2}{15} [(\ln 2J - 1.5)^{-1} + 3(\ln 2J - 0.5)^{-1}], \quad J > 15. \quad [12]$$

The relative viscosity η_r of the cylindrical micellar solution can be computed knowing the shape factor ν and the volume fraction ϕ of the surfactant micelles in solution using the empirical equation (25–27)

$$\eta_r = (\eta/\eta_{CMC}) = 1 + \nu_C \phi + k_1(\nu_C \phi)^2 + k_2(\nu_C \phi)^3. \quad [13]$$

The subscript C on the shape factor denotes the fact that the average micelle size \bar{g}_w and therefore, the corresponding shape factor ν depend on the total surfactant concentration. The relative viscosity is computed in relation to a solution at the CMC and it therefore accounts only for the contribution of the micelles and excludes that of the singly dispersed amphiphiles. The term $k_1(\nu_C \phi)^2$ accounts for the hydrodynamic interactions and the coefficient k_1 is estimated to be about 0.75 (27). The term $k_2(\nu_C \phi)^3$ arises due to direct micelle-to-micelle interactions and will be neglected for dilute surfactant solutions. The volume fraction ϕ of the micelles in solution can be calculated from the expression

$$\phi = (X - X_{CMC})(V_s/V_w) = (10/55.5 M_s)(C - C_{CMC})(V_s/V_w), \quad [14]$$

where V_s and V_w are the volumes of the surfactant molecule and of the water molecule, respectively, and C and C_{CMC} are the total surfactant concentration and the CMC expressed in units of (g/dl); M_s is the molecular

TABLE I

Analysis of Experimental Viscosity Data (13) for Dodecylammonium Chloride at 30°C and 0.15 M NaCl

C (g/dl)	η_r	$[\eta_c]$ (dl/g)	ν_c	\bar{g}_w/g_s	$K \times 10^{-8}$
0.3	1.0189	0.093	8.18	15.5	10.5
0.4	1.0340	0.111	9.77	18.8	10.6
0.5	1.0518	0.125	11.0	20.6	9.6
0.6	1.0723	0.138	12.14	22.2	9.0
0.8	1.1225	0.161	14.17	25.2	8.4
1.0	1.1887	0.186	16.37	28.5	8.4

Note. $C_{CMC} = 0.100$ g/dl, $M_S = 222$, $g_S = 57$, $l_0 = 16.8$ Å, $\delta = 6$ Å, $V_S/V_w = 14$. $[\eta] = 0.060$ dl/g estimated in Ref. (13). $\bar{g}_w/g_S = 18.26$ estimated in Ref. (13). $K = (9.5 \pm 1.0) \times 10^8$ our estimate.

weight of the surfactant. The volume V_S includes in addition to the volume of the surfactant, the volumes of adsorbed counterions and water of hydration at the surfactant head group. The value of V_S can be estimated from the experimental measurements of the relative viscosity η_r under conditions when only small spherical micelles form. For such a case the shape factor ν is 2.5 and knowing η_r and $(C - C_{CMC})$, one can use Eqs. [13] and [14] to estimate the ratio (V_S/V_w) .

The intrinsic viscosity is related to the shape factor by the expression

$$[\eta_C] = \nu_C \phi / (C - C_{CMC}), \quad [15]$$

where the subscript C is added to indicate that the intrinsic viscosity is a function of the concentration of the micelles, because of the concentration dependence of the average micellar size \bar{g}_w and thus of the shape factor ν_C . Equation [13] can be alternately expressed in terms of the intrinsic viscosity as

$$\eta_r = 1 + [\eta_C](C - C_{CMC}) + 0.75[\eta_C]^2(C - C_{CMC})^2. \quad [16]$$

All viscometric studies in literature use expressions similar to equation [16], but consider $[\eta]$ to be a constant given by

$$[\eta] = (\eta_r - 1)/(C - C_{CMC}) \quad \text{as } (C - C_{CMC}) \rightarrow 0. \quad [17]$$

Equation [17] commonly used for nonassociating macromolecular solutions assumes the existence of a single value for the intrinsic viscosity of cylindrical micelles at all surfactant concentrations. On the other hand, Eq. [16] requires a concentration-dependent intrinsic viscosity compatible with the concentration dependence of the average size of the micelles.

In this paper, the experimental viscosity data available in literature are used along with Eq. [16] to calculate the intrinsic viscosity $[\eta_C]$ as a function of the concentration of micelles in solution. The intrinsic viscosity so determined is independent of any assumptions concerning the rigidity or the flexibility of the large cylindrical micelles. From Eq. [15], the shape factor ν_C is determined. The corresponding average aggregation number \bar{g}_w of micelles treated as rigid rods is computed using Eqs. [9] to [12], as a function of the micellar concentration. Using the estimates of \bar{g}_w , the value of parameter K appearing in Eq. [5] is computed. A constant value for K at all surfactant concentrations implies that the treatment of cylindrical micelles as rigid rods agrees well with the two essential features of large micelles, namely, the dependence of the average micellar size on the square root of the concentration of micelles and the polydispersity of the micellar solution.

TABLE II

Analysis of Experimental Viscosity Data (13) for Dodecylammonium Chloride at 30°C and 0.20 M NaCl

C (g/dl)	η_r	$[\eta_c]$ (dl/g)	ν_c	\bar{g}_w/g_s	$K \times 10^{-9}$
0.3	1.055	0.256	22.53	34.0	5.20
0.4	1.098	0.299	26.31	38.3	4.53
0.5	1.152	0.338	29.74	42	4.13
0.6	1.214	0.370	32.56	44.5	3.73
0.8	1.372	0.429	37.75	49	3.26
1.0	1.588	0.487	42.86	54	3.10

Note. $C_{CMC} = 0.093$ g/dl, $M_S = 222$, $g_S = 57$, $l_0 = 16.8$ Å, $\delta = 6$ Å, $V_S/V_w = 14$. $[\eta] = 0.15$ dl/g estimated in Ref. (13). $\bar{g}_w/g_S = 51.8$ estimated in Ref. (13). $K = (3.9 \pm 0.8) \times 10^9$ our estimate.

ANALYSIS OF VISCOSITY DATA FROM THE LITERATURE

Data of Kushner et al. (13). These workers have carried out light-scattering and viscometric measurements on three cationic surfactant solutions at different concentrations of the electrolyte NaCl. Since large micelles are formed in solutions of dodecylammonium chloride containing 0.15, 0.20, 0.25, and 0.30 M NaCl, we have chosen the viscosity data obtained under these conditions for reevaluation. As described in the previous section, the concentration-dependent intrinsic viscosity $[\eta_C]$, the shape factor ν_c , the size of the micelle (\bar{g}_w/g_s), and the parameter K are computed and the results are presented in Tables I to IV. Shown also for comparison are the concentration-independent single values of intrinsic viscosity and micellar molecular weight estimated by the authors in their original paper. For all solutions, reasonably constant values of K over the range of surfactant concentrations are obtained. Small variations in K are inevitable because Eq. [5] for the concentration dependence of the micellar size is valid only at sufficiently high micelle concentration compared to the CMC. A variation of less than 10 to 15 percent in the estimate for K is obtained which implies less than 5 to 8 percent deviation in the size of the micelles compared to the theoretical predictions. The results in Tables I to IV suggest that for these solution conditions, the

TABLE III

Analysis of Experimental Viscosity Data (13) for Dodecylammonium Chloride at 30°C and 0.25 M NaCl

C (g/dl)	η_r	$[\eta_C]$ (dl/g)	ν_c	\bar{g}_w/g_s	$K \times 10^{-10}$
0.3	1.116	0.519	45.67	55	1.41
0.4	1.218	0.621	54.65	62	1.21
0.6	1.538	0.811	71.37	75	1.08
0.8	2.134	1.035	91.08	87	1.05

Note. $C_{CMC} = 0.093$ g/dl, $M_S = 222$, $g_s = 57$, $l_0 = 16.8$ Å, $\delta = 6$ Å, $V_S/V_w = 14$. $[\eta] = 0.33$ dl/g estimated in Ref. (13). $\bar{g}_w/g_s = 88.9$ estimated in Ref. (13). $K = (1.20 \pm 0.15) \times 10^{10}$ our estimate.

TABLE IV

Analysis of Experimental Viscosity Data (13) for Dodecylammonium Chloride at 30°C and 0.30 M NaCl

C (g/dl)	η_r	$[\eta_C]$ (dl/g)	ν_c	\bar{g}_w/g_s	$K \times 10^{-10}$
0.3	1.250	1.001	88.09	84.5	3.24
0.4	1.545	1.319	116.07	99	3.05
0.5	2.023	1.634	143.79	113	3.02

Note. $C_{CMC} = 0.085$ g/dl, $M_S = 222$, $g_s = 57$, $l_0 = 16.8$ Å, $\delta = 6$ Å, $V_S/V_w = 14$. $[\eta] = 0.45$ dl/g estimated in Ref. (13). $\bar{g}_w/g_s = 142.2$ estimated in Ref. (13). $K = (3.1 \pm 0.1) \times 10^{10}$ our estimate.

treatment of micelles as rigid rods agrees quite well with the theoretically anticipated properties of large micelles. Furthermore, the magnitude of parameter K estimated from the viscometric data compares very well with other known estimates for rodlike micellar solutions (Table V). It may be noted that using the same viscosity data obtained by Kushner *et al.* (13), but treating the intrinsic viscosity and micelle size as concentration independent quantities, diametrically opposite conclusions, namely, that large micelles should be flexible have been reached in literature (16, 18).

Data of Ozeki and Ikeda (16). Recently, viscometric (16) and light-scattering (28) measurements of dodecyltrimethylammonium chloride solutions at various concentrations of electrolyte NaCl have been carried out by Ozeki and Ikeda. In these studies the intrinsic viscosities of the micellar solutions and the micellar molecular weights are determined as functions of the added electrolyte concentration but as independent of the concentration of micelles. These estimates have been used to arrive at the conclusion that the large micelles are flexible but not rigid.

We have reevaluated the experimental viscosity data presented in Ref. (16). Illustrative results are shown here for solutions containing 1, 2, and 4 M NaCl in Tables VI, VII, and VIII, respectively. At 1 M NaCl, the treatment of viscosity data assuming micelles are rigid rods yields a constant value of the

TABLE V
Comparison of Available Estimates for the Parameter K

Surfactant system	K	Technique	Ref.
Hexadecyltrimethylammonium bromide in 0.178 M KBr	2.71×10^{10}	Light scattering	(4)
Hexadecylheptoxyethylene glycol monoether at 25°C	2.7×10^{10}	Light scattering	(4)
Tetradecylhexoxyethylene glycol monoether at 25°C	1.33×10^{10}	Light scattering	(4)
Diocanoyl lecithin at 25°C and in 0.2 M Lil	1.6×10^{10}	Light scattering	(8, 9)
Sodium dodecyl sulfate at 30°C and in 0.8 M NaCl	$(3.5 \pm 0.6) \times 10^8$	Light scattering	(10)
Dodecylammonium chloride at 30°C and in 0.15 M NaCl	$(9.5 \pm 1.0) \times 10^8$	Viscosity	This work
Dodecylammonium chloride at 30°C and in 0.20 M NaCl	$(3.9 \pm 0.8) \times 10^9$	Viscosity	This work
Dodecylammonium chloride at 30°C and in 0.25 M NaCl	$(1.20 \pm 0.15) \times 10^{10}$	Viscosity	This work
Dodecylammonium chloride at 30°C and in 0.30 M NaCl	$(3.10 \pm 0.1) \times 10^{10}$	Viscosity	This work
Dodecylammonium trifluoroacetate at 25°C	$(4.80 \pm 0.5) \times 10^9$	Viscosity	This work
Dodecyltrimethylammonium chloride at 25°C and in 1 M NaCl	$(6.60 \pm 0.6) \times 10^7$	Viscosity	This work
Dodecyltrimethylammonium chloride at 25°C and in 2 M NaCl	$(1.70 \pm 0.6) \times 10^9$	Viscosity	This work

parameter K thus demonstrating good agreement with the theoretically anticipated features of rodlike micellar solutions. In solutions containing 2 M NaCl, while the average size of the micelles treated as rigid rods increases with increasing surfactant concentration, the magnitude of this increase in size is somewhat smaller than that predicted by the theory. This is reflected in the larger variability of about 35 percent for the estimated value of K which implies a deviation in micelle size of up to about 16 percent from the theoretical predictions. For electrolyte concentrations above 2 M NaCl, such as at 4 M NaCl, the estimated size of the micelles treated as rigid rods is practically independent of the surfactant concentration and therefore, the values of parameter K show a rapid decrease with increasing surfactant concentration. This deviation from the theoretically predicted behavior exhibited by 4 M NaCl solution is examined later.

Data of Hoffman et al. (17). These authors have examined the solution behavior of two ionic perfluorodetergents using different techniques and have found that dodecylam-

TABLE VI
Analysis of Experimental Viscosity Data (16) for Dodecyltrimethylammonium Chloride at 25°C and 1 M NaCl

C (g/dl)	η_r	$[\eta_c]$ (dl/g)	ν_c	\bar{g}_w/g_s	$K \times 10^{-7}$
0.5	1.022	0.046	3.56	6	5.97
1.0	1.058	0.057	4.41	8.4	6.36
1.5	1.109	0.069	5.34	10.5	6.93
2.0	1.174	0.079	6.11	12.2	7.19
2.5	1.252	0.088	6.81	13.6	7.26
3.0	1.345	0.096	7.43	14.8	7.25

Note. $C_{CMC} = 0.026$ g/dl, $M_s = 251$, $g_s = 57$, $l_0 = 16.8$ Å, $\delta = 6$ Å, $V_s/V_w = 18$. $[\eta] = 0.039$ dl/g estimated in Ref. (16). $\bar{g}_w/g_s = 3.914$ estimated in Ref. (16). $K = (6.6 \pm 0.6) \times 10^7$ our estimate.

moniumtrifluoroacetate forms rodlike micelles. Using the viscosity data at 25°C reported by the above authors, the concentration dependence of the intrinsic viscosity and of the average size of the micelles are computed and the results are shown in Table IX. It is found that the parameter K remains constant over the range of surfactant concentrations studied. This again demonstrates good agreement between the rigid rod model for large micelles and the theoretically anticipated properties of large micelles.

DISCUSSION

The theories for large micelles (4, 8–12) predict that the average size of the micelles should increase in proportion to the square root of the micellar concentration and that the micellar solution should be polydisperse. From the results presented in Tables I to IX, we find that for most of the surfactant solutions, constant values for the parameter K are obtained. This signifies that the treatment of viscosity data assuming that the micelles are rigid is in very good agreement with the theoretical predictions. Only in a few cases (Table VIII), the concentration dependence of the micellar size obtained from the viscosity data deviates from the theoretical predictions. As a matter of fact for the 4 M NaCl solution of dodecyldimethylammonium

TABLE VII

Analysis of Experimental Viscosity Data (16) for Dodecyldimethylammonium Chloride at 25°C and 2 M NaCl

C (g/dl)	η_r	$[\eta_c]$ (dl/g)	ν_c	\bar{g}_w/g_s	$K \times 10^{-9}$
1.0	1.54	0.419	32.43	45.3	2.26
1.5	2.08	0.476	36.84	49	1.76
2.0	2.80	0.514	39.78	51.5	1.46
2.5	3.70	0.541	41.87	53	1.23
3.0	4.78	0.561	43.42	54.5	1.09

Note. $C_{CMC} = 0.016$ g/dl, $M_S = 251$, $g_S = 57$, $l_0 = 16.8$ Å, $\delta = 6$ Å, $V_S/V_w = 18$. $[\eta] = 0.17$ dl/g estimated in Ref. (16). $\bar{g}_w/g_S = 26.60$ estimated in Ref. (16). $K = (1.7 \pm 0.6) \times 10^9$ our estimate.

TABLE VIII

Analysis of Experimental Viscosity Data (16) for Dodecyldimethylammonium Chloride at 25°C and 4 M NaCl

C (g/dl)	η_r	$[\eta]$ (dl/g)	ν_c	\bar{g}_w/g_s	$K \times 10^{-10}$
0.25	1.75	2.184	169.04	125	6.96
0.50	3.20	2.366	183.13	131	3.83
0.75	5.24	2.420	187.31	133	2.63
1.00	7.68	2.403	185.99	132.5	1.96
1.25	10.31	2.345	181.50	130.4	1.52
1.50	13.0	2.267	175.47	127.6	1.21

Note. $C_{CMC} = 0.0045$ g/dl, $M_S = 251$, $g_S = 57$, $l_0 = 16.8$ Å, $\delta = 6$ Å, $V_S/V_w = 18$. $[\eta] = 1.10$ dl/g estimated in Ref. (16). $\bar{g}_w/g_S = 205.6$ estimated in Ref. (16).

chloride (Table VIII), the estimated micelle size remains practically independent of the micellar concentration. We examine below whether this disagreement from theory can be attributed to any of the following causes: (i) micellar polydispersity influences the solution viscosity, (ii) the theoretical concentration dependence of the micellar size given by Eq. [5] is altered due to intermicellar interactions, and (iii) the large micelles are flexible and therefore they influence the solution viscosity differently compared to the rigid rods.

The influence of polydispersity on micellar solution viscosity has been examined by us (19) using an empirical equation that has been used (29–31) to estimate the viscosity of polydisperse colloidal suspensions. The empirical equation considers the relative viscosity of the polydispersed solution to be the geometric sum of the relative viscosities of the various constituent fractions. The relative viscosity of the polydispersed micellar solution calculated in this manner for \bar{g}_w/g_S up to 25 differs by less than four percent from that calculated assuming monodispersed micelles having size \bar{g}_w . Even for large \bar{g}_w/g_S up to 120, the difference between the relative viscosities calculated assuming polydispersity and assuming monodispersity do not exceed by more than 20 percent. The results presented in this paper which show good agree-

TABLE IX

Analysis of Experimental Viscosity Data (17) for
Dodecylammoniumtrifluoroacetate at 25°C

C (g/dl)	η_r	$[\eta]$ (dl/g)	ν_c	\bar{g}_w/g_s	$K \times 10^{-9}$
0.449	1.053	0.225	18.68	31	4.91
0.598	1.120	0.280	23.24	36.5	4.29
0.748	1.265	0.415	34.45	47	5.22
0.897	1.411	0.474	39.34	51	4.85
1.196	1.948	0.643	53.37	62	5.04
1.495	2.934	0.829	68.81	72	5.25

Note. $C_{CMC} = 0.202$ g/dl, $M_s = 299$, $g_s = 57$, $l_0 = 16.8$ Å, $\delta = 6$ Å, $V_s/V_w = 20$. $K = (4.8 \pm 0.5) \times 10^9$ our estimate.

ment with the theory also reinforce the view that the influence of polydispersity on solution viscosity is rather small. Furthermore, from the data in Table VIII, we note that the intrinsic viscosities are practically concentration independent. Any correction for polydispersity, therefore, would influence the micellar sizes at all the concentrations equally. Consequently, the influence of polydispersity cannot modify the concentration dependence of the micellar size and lead to agreement with the theory.

The second explanation suggests that the average micellar size may have a weaker dependence on micelle concentration than that given by Eq. [5] and may even become independent of micelle concentration when the micelles are very large, due to intermicellar interactions. Equation [1] for the micelle size distribution and all the subsequent thermodynamic relations including Eq. [5] assume that there are no interactions among micelles. This assumption is quite reasonable for dilute surfactant solutions when small micelles are formed. In more concentrated solutions, the intermicellar interactions are likely to be important. Further, if very large micelles form in dilute solutions, then the intermicellar interactions may become important even in dilute solutions. Such behavior is well known for polymer solutions

in which as the polymer size is increased, the intermolecular interactions begin to be important in increasingly more dilute solutions. Alternate thermodynamic equations to replace Eqs. [1] through [6] have to be developed taking into account intermicellar interactions, before this explanation can be fully evaluated. At present, we only note that the data of Table VIII is not in disagreement with such an explanation.

The last explanation assumes that large micelles are flexible. Even if this assumption is valid, it would influence the estimated micellar sizes of Table VIII equally at all surfactant concentrations because the intrinsic viscosities are practically equal. This therefore cannot lead to agreement with theory which requires that the micellar size vary in proportion to the square root of the micelle concentration.

From the above arguments it appears that the deviation from theory exhibited by data in Table VIII is most likely caused by intermicellar interactions which modify the concentration dependence of the micelle size from that given by Eq. [5].

The most important result from the present calculations, however, is the finding that the large micelles can be satisfactorily treated as rigid rods. Experimental data for intrinsic viscosities up to 1.7 dl/g or estimated weight average aggregation numbers \bar{g}_w up to 6400 (i.e., \bar{g}_w/g_s up to 115) have been treated using the rigid rod model. Viscosity data interpreted in this manner show that the average size of the large micelles increases in proportion to the square root of the micelle concentration as is anticipated by theory. These conclusions remain fully valid even if the parameters l_0 , δ , and V_s/V_w used in the computations are assigned values different from those considered here. Earlier treatments of viscometric measurements fail to account for the concentration dependence of the intrinsic viscosity and of the average size of the micelles and consequently lead to the conclusion that large micelles are flexible. In contrast, we conclude that in general, large

micelles can be treated more accurately as rigid rods rather than as flexible rods or coils.

APPENDIX: COMPARISON OF THERMODYNAMIC MODELS FOR LARGE MICELLES

Mukerjee's (4) model is the first thermodynamic theory suggested for large micelles and is based on the multiple-equilibrium description of the micellization process. In this model, all the stepwise association equilibrium constants are considered equal (K_1) except for the hypothetical dimerization equilibrium constant (K_2). When the micelle size \bar{g}_w is large and when the micelle concentration is significantly larger than that of the singly dispersed surfactant, Mukerjee has shown that

$$\bar{g}_w = 2(K_1/K_2)^{1/2} \times [(X - X_{CMC})/X_{CMC}]^{1/2}. \quad [A-1]$$

He has also shown that when the above equation is valid, then automatically the polydispersity index, \bar{g}_w/\bar{g}_n , assumes a value of 2.

Tausk and Overbeek (8, 9) have presented a modification of the above equation, again starting from the framework of the multiple-equilibrium description of micellization. Here it is assumed that no micelles are present up to an aggregation number g_0 beyond which the stepwise association constant K_1 is assumed to be constant for all the association equilibria. The monomer-micelle association equilibrium constant for the smallest micelle of size g_0 is designated to be $K_2^{g_0-1}$. When large micelles form and at sufficiently large micelle concentrations compared to that of the monomer, it has been shown that

$$\bar{g}_w = 2(K_1/K_2)^{[g_0-1]/2} \times [(X - X_{CMC})/X_{CMC}]^{1/2}. \quad [A-2]$$

Again the polydispersity index automatically assumes a value of 2. The equation of Tausk and Overbeek reduces to that developed by Mukerjee if g_0 is taken to be 2.

Israelachvili *et al.* (10) starting from the

micelle size distribution Eq. [1], proposed the following expression for the standard free energy per molecule of a large cylindrical micelle

$$\begin{aligned} \mu_g^0 &= \mu_\infty^0 + \alpha kT/g \quad \text{for } g > g_0 \\ &= \infty \quad \text{for } 1 < g < g_0. \end{aligned} \quad [A-3]$$

The above equation assumes that micelles below an aggregation number g_0 are absent. When large micelles form and when the total micelle concentration is sufficiently larger than that of the monomer, it has been shown that the average micelle size \bar{g}_w is given by

$$\bar{g}_w = g_0 + 2[(X - X_1)e^\alpha]^{1/2}. \quad [A-4]$$

The above equation is formally equivalent to that developed by Mukerjee (14) if e^α is identified with $(K_1/K_2 X_{CMC})$.

Mazer *et al.* (11, 12) presented an analysis of large micelles along the lines considered by Israelachvili *et al.* [10]. In Eq. [A-3], μ_∞^0 is replaced by μ_c^0 , g_0 by g_s , and α by $g_s(\mu_s^0 - \mu_c^0)/kT$. The concentration dependence of the average micellar size is then obtained as

$$\bar{g}_w = g_s + 2[K(X - X_{CMC})]^{1/2}, \quad [A-5]$$

where

$$K = \exp[-g_s(\mu_c^0 - \mu_s^0)/kT]. \quad [A-6]$$

We have used Eq. [A-5] to represent the dependence of micelle size on micelle concentration, recognizing the equivalence between Eqs. [A-1], [A-2], [A-4], and [A-5]. From Eq. [A-5] it is evident that for large micelles, $\bar{g}_w = 10^3$ to 10^4 , to form at reasonable micellar concentrations $(X - X_{CMC}) = 10^{-5} \sim 10^{-3}$, K should have values in the range 10^8 to 10^{11} .

REFERENCES

1. Tanford, C., "The Hydrophobic Effect." Wiley, New York, 1973.
2. Mukerjee, P., in "Micellization, Solubilization and Microemulsions" (K. L. Mittal, Ed.), Vol. 1, p. 171. Plenum, New York, 1977.
3. Nagarajan, R., and Ruckenstein, E., *J. Colloid Interface Sci.* **71**, 580 (1979).

4. Mukerjee, P., *J. Phys. Chem.* **76**, 565 (1972).
5. Debye, P., and Anacker, E. W., *J. Phys. Colloid Chem.* **55**, 644 (1951).
6. Elworthy, P. H., and Macfarlane, C. B., *J. Chem. Soc.* 907 (1963).
7. Balmbra, R. R., Clunie, J. S., Corkill, J. M., and Goodman, J. F., *Trans. Faraday Soc.* **60**, 979 (1964).
8. Tausk, R. J. M., Oudshoorn, C., and Overbeek, J. Th. G., *Biophys. Chem.* **2**, 53 (1974).
9. Tausk, R. J. M., and Overbeek, J. Th. G., *Biophys. Chem.* **2**, 175 (1974).
10. Israelachvili, J. N., Mitchell, D. J., and Ninham, B. W., *Trans. Faraday Soc.* **72**, 1525 (1976).
11. Missel, P. J., Mazer, N. A., Benedek, G. B., Young, C. Y., and Carey, M. C., *J. Phys. Chem.* **84**, 1044 (1980).
12. Missel, P. J., Mazer, N. A., Carey, M. C., and Benedek, G. B., preprint of paper presented at the International Symposium on Solution Behavior of Surfactants, Potsdam, NY, 1980.
13. Kushner, L. M., Hubbard, W. D., and Parker, R. A., *J. Res. Natl. Bur. Stand.* **59**, 113 (1957).
14. Ekwall, P., Mandell, L., and Solyom, P., *J. Colloid Interface Sci.* **35**, 519 (1971).
15. Guveli, D. E., Kayes, J. B., and Davis, S. S., *J. Colloid Interface Sci.* **72**, 130 (1979).
16. Ozeki, S., and Ikeda, S., *J. Colloid Interface Sci.* **77**, 219 (1980).
17. Hoffman, H., Platz, G., and Ulbricht, W., *J. Phys. Chem.* **85**, 1418 (1981).
18. Stigter, D., *J. Phys. Chem.* **70**, 1323 (1966).
19. Nagarajan, R., Shah, K. M., and Hammond, S., *Colloids Surf.* **4**, 147 (1982).
20. Tanford, C., *J. Phys. Chem.* **78**, 2469 (1974).
21. Ruckenstein, E., and Nagarajan, R., *J. Phys. Chem.* **79**, 2622 (1975).
22. Tanford, C., "Physical Chemistry of Macromolecules." Wiley, New York, 1961.
23. Kuhn, W., Kuhn, H., and Buchner, P., in "Ergebnisse der Exakten Naturwissenschaften" (S. Flugge and G. Trendelenburg, Eds.), Vol. 25, p. 1-108. Springer-Verlag, Berlin, 1951.
24. Simha, R., *J. Phys. Chem.* **44**, 25 (1940).
25. Huggins, M. L., *J. Amer. Chem. Soc.* **64**, 2716 (1942).
26. Simha, R., *J. Res. Natl. Bur. Stand.* **42**, 409 (1949).
27. Matheson, Jr., R. R., *Macromolecules* **13**, 643 (1980).
28. Ikeda, S., Ozeki, S., and Tsunoda, M., *J. Colloid Interface Sci.* **73**, 27 (1980).
29. Mooney, M., *J. Colloid Sci.* **6**, 162 (1951).
30. Eveson, G. F., in "Rheology of Disperse Systems" (C. C. Mill, Ed.), p. 61. Pergamon Press, London, 1959.
31. Parkinson, C., Matsumoto, S., and Sherman, P., *J. Colloid Interface Sci.* **33**, 150 (1970).