The Application of the Archibald Ultracentrifugal Method to the Determination of the Micellar Molecular Weight of the Anionic Surface Active Agents

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Although the sedimentation equilibrium method of ultracentrifugation gives a reliable molecular weight, it requires a very long time to attain the equilibrium state. Archibald[1] has suggested procedures by which molecular weight can be determined without waiting for the equilibrium state. As he has shown, the sedimentation equilibrium equation always holds at the meniscus and at the bottom of a liquid column within the cell. The equations are given by:

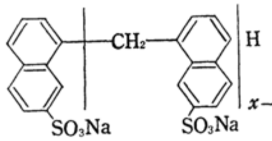
$$M_m=\frac{RT}{(1-\bar{v}\rho_0)\omega^2}\left(\frac{\mathrm{d}c/\mathrm{d}r}{rc}\right)_m \qquad (1)$$

for the meniscus, and

$$M_b=\frac{RT}{(1-\bar{v}\rho_0)\omega^2}\left(\frac{\mathrm{d}c/\mathrm{d}r}{rc}\right)_b \qquad (2)$$

for the bottom, where M is the molecular weight; R, the gas constant; T, the absolute temperature; $\bar{v}$, the partial specific volume of the solute; ρ_0 the density of the solvent; ω, the angular velocity; c, the solute concentration; r, the distance measured from the axis of the rotor to the meniscus or bottom of the liquid column within the cell, and the suffixes m and b, the meniscus and bottom of the liquid column respectively.

The Archibald ultracentrifugal method has been increasingly applied to the determination of the micellar weights of nonionic surface active agents[2,3] in an aqueous solution. It is worthwhile to investigate whether or not this method can also be applied to the determination of the miceller weight of anionic surface active agents. The purpose of the present investigation, therefore, is to confirm the applicability of the Archibald method to anionic surface active agents. The systems studied in the present investigation are the aqueous solution of sodium dodecyl sulfate (SDS) and the formalin condensates of sodium β-naphthalene sulfonate (β-NF). The latter compounds have the formula:[4]



where x is the number of naphthalene nuclei, 1, 2, 3, ……, 8, 9.5 (average) and 13.5 (average).

Experimental

Apparatus.—The experiments were performed in a Hitachi Analytical Ultracentrifuger, UCA-1 type (maximum speed 60000 r.p.m.), equipped with a Schlieren cylindrical lens system. The temperature was measured with a radiation thermocouple provided a continuous indication of the temperature of the base of the rotor, with an accuracy of ±0.1°C. To make the photographs more clear a piece of human hair was used for the inclined slit.

For each test a given sample of a definite concentration in water or in a sodium chloride solution was placed in a conventional cell. At a fixed speed of rotation, six photographs of the sedimentation pattern were taken at intervals of ten minutes. At the same time, the corresponding temperatures of the rotor were measured, and their average value was used for the calculations. The temperature was 20±3°C.

The patterns are shown in Fig. 1. $\mathrm{d}c/\mathrm{d}r$ corresponds to the vertical axis, since in our present experimental concentration we assume that $\mathrm{d}c/\mathrm{d}r$ is proportional to $\mathrm{d}n/\mathrm{d}r$ (n: refractive index). r corresponds to the horizontal axis. By measuring the area under the curve of the meniscus or bottom, it is possible to obtain a numerical value proportional to the decreased or increased concentration. Similarly, three patterns obtained from the boundary-forming cell give the average value proportional to the initial concentration by measuring the area under the curve. Thus, the apparent concentration at the meniscus and bottom at every interval of time is determined. The molecular weights at any one time are given by Eqs. 1 and 2, which represent the molecular weights at both the meniscus and bottom of the cell.[5,6] We denote these as

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[1] W. J. Archibald, *J. Phys. and Colloid Chem.*, **51**, 1504 (1949).

[2] C. W. Dwiggins, Jr., R. J. Bolen and H. N. Dunning, *J. Phys. Chem.*, **64**, 1175 (1960).

[3] F. Tokiwa and T. Isemura, This Bulletin 35, 1737 (1962).

[4] K. Hattori and Y. Tanino *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 55 (1963).

[5] G. Kegeles, S. M. Klainer and W. J. Salem, *J. Phys. Chem.*, **61**, 1286 (1957).

[6] H. K. Schachman, "Ultracentrifugation in Biochemistry," Academic Press, New York and London (1959).

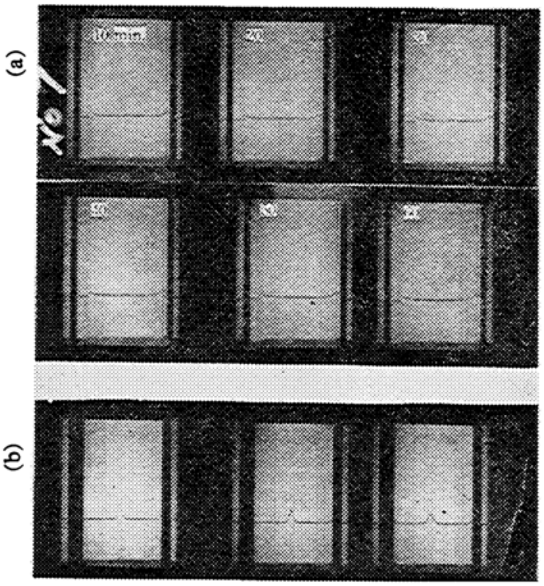

Fig. 1. Photographs for Archibald method.

(a) Pictures correspond to 10, 20, 30, 40, 50 and 60 min. after attaining 15200 r.p.m.

(b) Pictures from boundary-forming cell. By measuring the area it is possible to obtain the concn. of the initial solution, c_0.

$M_m(t)$ and $M_b(t)$ respectively. $M_m(t)$ or $M_b(t)$ tends to decrease or increase with time according as the solution is non-ideal or polydisperse. To obtain the appearent weight-average molecular weights of the solutes, M_0, $M_m(t)$ or $M_b(t)$ should be extrapolated to time zero.

$M_m(t)$ was exclusively used to obtain reliable data from the meniscus rather than the bottom. There is a possibility of an increase in micellar weight upon the addition of silicone oil[7] for the formation of the bottom surface.

The partial specific volume was calculated by the equation:

$$\bar{v}=\frac{1}{\rho_0}\left[1-\frac{\rho-\rho_0}{W}\right] \tag{3}$$

Here ρ is the density of a solution containing W g. solute in 1 ml., and ρ_0 is the density of the solvent. The densities were determined by the picnometer of Lipkin et al.[8]

Materials. — *Sodium Dodecyl Sulfate (SDS).* — The dodecyl alcohol used for preparing sodium dodecyl sulfate was purified by fractional distillation under reduced pressure several times. It contained no homologues detectable by gas chromatographical analysis, and its hydroxyl value was found to be 301.0 (calcd. 301.1). Sodium dodecyl sulfate was prepared by the method of Dreger et al.,[9] followed by repeated recrystallization from ethanol and by extraction with petroleum ether. The aqueous solution of the purified propuct showed no minimum point in its surface tension-concentration curve.

The partial specific volume of SDS was found to be 0.825 in water and 0.855 in a 0.01~0.1 M sodium chloride solution.

The Condensates of Sodium β-Naphthalene Sulfonate (β-NF).—These compounds with $x=1\sim8$ were purified by a method previously reported.[4] The purity was confirmed by "one spot" on the paper chromatogram analysis. β-NF's with $x=9.5$ and 13.5 were synthesized by the usual methods and were not purified further except by dialysis to remove lower polymers. Their molecular weights were determined by infrared spectra.[10] Table I summarizes the partial specific volumes of β-NF in water and in a 0.1 M sodium chloride solution.

TABLE I. PARTIAL SPECIFIC VOLUME OF β-NF (at 25°C, concn. 1%)

x	Distilled water	0.1 M Sodium chloride
1	0.637	0.612
2		0.591
3		0.576
4		0.621
5		0.595
6		0.635
7		0.627
8		0.600
9.5		0.597
13.5	0.632	0.635
Average value	0.634	0.610

Results and Discussion

The determination of the micellar molecular weights of the ionic-surface active agent by the Archibald method has not previously been reported. The reason seems to have been that the micelle of ionizable molecules is disintegrated by the increasing repulsion between ionic groups because the micelles sediment faster, leaving the counter ions behind.

The Archibald method may be applicable to the determination of the micellar molecular weight if the disintegration of the micelle is prevented by adding a neutral electrolyte to the solution, although the micellar weight might be dependent on the concentration of the added electrolyte.

The Micellar Molecular Weight of Sodium Dodecyl Sulfate. — Table II summarizes the micellar molecular weights, M_0, of SDS at different concentrations in water or in a sodium chloride solution. In the absence of sodium chloride, SDS has a very low number of association, indicating the disintegration of the micelle mentioned above in the ultracentrifugal field.

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[7] S. M. Klainer and G. Kegeles, *Arch. Biochem. Biophys.*, **63**, 247 (1956).

[8] M. R. Lipkin, J. A. Davison, W. T. Harvey and S. S. Kurty, *Ind. Eng. Chem. Anal. Ed.*, **16**, 55 (1944).

[9] E. E. Dreger, G. I. Keim, G. D. Miles, L. Shedlovsky and J. Ross, *Ind. Eng. Chem.*, **36**, 610 (1944).

[10] K. Hattori and K. Konishi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 59 (1963).

TABLE II. MICELLAR MOLECULAR WEIGHTS OF SDS (M_0)

Exp. No.	Concn. of SDS, %	Concn. of NaCl, M	Temp. °C	Micellar M. W.	No. of Association
1	1.00	0.00	21.1	2.06×10^3	7.1
12	0.65	0.00	19.2	3.80×10^3	13
2	0.50	0.00	20.8	7.05×10^3	24
3	0.25	0.00	21.2	8.00×10^3	28
13	0.20	0.00	22.7	3.90×10^3	15
7	1.00	0.01	23.0	6.64×10^3	23
14	2.00	0.10	21.3	1.41×10^4	49
4	1.00	0.10	19.6	1.32×10^4	46
5	0.50	0.10	18.0	2.37×10^4	82
6	0.25	0.10	19.4	3.37×10^4	117
11	0.10	0.10	20.9	1.41×10^4	49
7	1.00	0.20	23.4	2.50×10^4	87

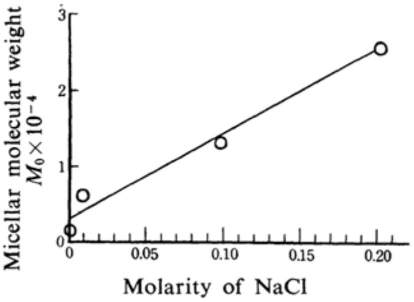

Fig. 2. Plots of micellar molecular weight of SDS as a function of molarity of sodium chloride. Concn. of SDS, 1.00%.

McBain and Hutchinson[11] are of the opinion that the micellar molecular weight of SDS is not changed by the addition of excess sodium chloride, that the effective volume of the micelle is enlarged, and that solubilizing power increases as the charge decreases. It is expected that the micellar molecular weight of SDS is obtainable in the presence of a neutral electrolyte. As Fig. 2 shows, however, the M_0 of a 1.00% SDS solution is proportional to the concentration of sodium chloride and, within the range of concentration of sodium chloride studied, the micellar molecular weight has no tendency to attain any limiting value.

The published values of the micellar molecular weight of SDS are very diverse, and the number of association, n, ranges over 40 to 80, as follows: 1.15×10^4 ($n=40$),[12] 1.14×10^4($n=40$),[13] 2.05×10^4($n=71$),[14] 2.3×10^4($n=79$)[15] and 1.80×10^4($n=62$)[16] are obtained by light scattering; $1.12\sim2.02\times10^4$ ($n=39\sim70$),[17] by diffusion and 1.70×10^4 ($n=57$),[18] by small angle X-ray scattering.

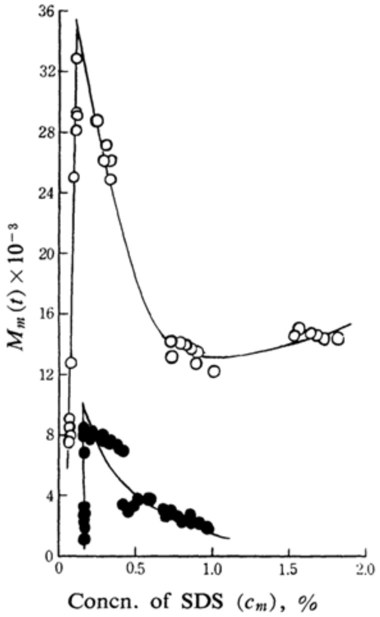

Fig. 3. Micellar molecular weight $M_m(t)$ as a function of the concn. of SDS. The concns. of SDS denote c_m at any time in the centrifugal run.

○: in 0.1 M sodium chloride solution
●: in water

Figure 3 shows the changes of $M_m(t)$ with the concentration of SDS at the meniscus, which varies with the time of the centrifugal run. It is clear that the numbers of association are varied from 40 to 80 at concentrations of more than 0.5% SDS in a sodium chloride solution. In the absence of sodium chloride, the numbers of association are much

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[11] M. E. L. McBain and E. Hutchinson, "Solubilization and Related Phenomena," Academic Press Inc., Publishers New York (1955), p. 176.

[12] H. V. Tarter, *J. Colloid Sci.*, **14**, 115 (1959).

[13] L. M. Kushner and W. D. Huffard, *J. Colloid Sci.*, **10**, 429 (1955).

[14] H. V. Tarter and A. C. M. Lelong, *J. Phys.C hem.*, **59**, 1185 (1955).

[15] J. M. Rhillips and J. K. Mysels, ibid., **59**, 325 (1955).

[16] L. H. Princen and J. K. Mysels, *11th Technical Report Project (NR)* 356-254, *Office of Naval Research* (1958).

[17] E. Hutchinson and J. C. Melrose, *Z. Phys. Chem.*, [NF] **2**, 117 (1954).

[18] W. Philippoff, *Discussions Faraday Soc.*, **11**, 96 (1951).

smaller. Below the concentration of 0.5% SDS, the curves of the numbers of association vs. concentration abruptly show a sharp maximum point. The concentrations of SDS at a sharp maximum point are 0.16% and 0.13% in water and in 0.1 M sodium chloride respectively. These values agree with the reported values for critical micelle concentration (CMC).[19,20] Clearly the addition of sodium chloride lowers the CMC of SDS. Tartar[12] and Kolthoff[19] reported that the CMC of SDS decreased from 0.25% to 0.174∼0.177% upon the addition of 0.1 M sodium chloride. Moreover, it is noted that above the CMC the slope of the linear relationship between $M_m(t)$ and time is positive, while below the CMC its slope is negative. Figure 4 illustrates that $M_m(t)$ increases with time above the CMC but decreases below the CMC.*

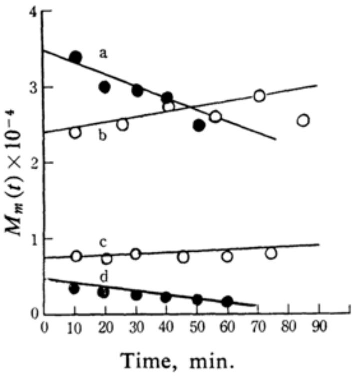

Fig. 4. Plots for $M_m(t)$ vs. time of centrifugation.

a : SDS 0.25%, NaCl 0.1 M
b : SDS 0.50%, NaCl 0.1 M
c : SDS 0.50%, NaCl (not contained)
d : SDS 0.20%, NaCl (not contained)

As Fujita et al.[21] have pointed out, $M_m(t)$ or $M_b(t)$ is a function of time. They also pointed out that the $M_m(t)$ of polystyrene in methyl ethyl ketone increased with time and that $M_b(t)$ decreased in an approximately linear fashion, but that they could be extrapolated to give the same intercept at $t=0$ in agreement with the theoretical requirement. Whether the slope of the $M_m(t)$-time curve is positive or negative depends on either the non-ideality or the polydispersity of the solution. It is supposed that non-ideality is predominant in the SDS solution above the CMC but the polydispersity is predominant below the CMC.

In the concentration of the critical micelle region, as Fig. 3 shows, it is necessary for us to handle with care a detailed treatment of the behavior by means of thermodynamic and hydrodynamic argument. However, it is very difficult to ascribe these deviations from the ideality to any non-ideality of the solute accompanied not only by the change of equilibrium between the micelle and the free ion but also by the disintegration of the micelle at the ultracentrifugal field. Goldberg[22] and Fujita et al.[21] have pointed out that in the application of the Archibald method the chemical potential is expressed in terms of both the concentration and the activity coefficient, γ, of the solute. For simplicity of theoretical development, they considered only two component systems, a homogeneous solute and a solvent. For such a solution the equation reduces to:

$$1/M_0 = 1/M_W + \boldsymbol{B}c + \text{higher terms in } c \quad (4)$$

where the coefficient $\boldsymbol{B}$ refers to the initial slope of $\ln \gamma$ at $c=0$ and, hence, is independent of the concentration, and M_W is the weight-average melecular weight. This equation indicates that a plot for $1/M_0$ vs. c allows an evaluation of M_W from its intercept at $c=0$ $\boldsymbol{B}$ from its initial slope. $\boldsymbol{B}$ corresponds to the second virial coefficient of light scattering. Fujita et al. have pointed out that for polystyrene in methyl ethyl ketone the plots for $1/M_0$ vs. concentration deviate from a straight line at relatively low concentrations and increase sharply with a further increase in c. This steep upward curvature suggests that the third and higher terms in the above equation would be quite different from those in the equation derived from the theory of light scattering.

In non-ideal solutions, the extended form of the Svedberg equation[23] reduces to:

$$M = \frac{\boldsymbol{R}T\mathrm{s}}{D(1-\bar{v}\rho)}\left[1-\frac{\mathrm{d}\ln\gamma}{\mathrm{d}\ln c}\right] \quad (5)$$

At an infinite dilution, the term in brackets becomes unity. Creeth[24] has shown that in a thallous sulfate-water system, $\mathrm{d}\ln\gamma/\mathrm{d}\ln c$ is positive within the range of his experimental concentration. This discrepancy between Eq.

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[19] I. M. Kolthoff and W. J. Stricks, *J. Phys. and Colloid Chem.*, **52**, 915 (1948).

[20] J. Powney and C. C. Addison, *Trans. Faraday Soc.*, **33**, 1243, 1253 (1937).

* The concentrations described in Fig. 4 are those for the prepared samples. In the coures of the centrifugal run the solute sediments partially form the meniscus. Accordingly, the concentration of SDS at the meniscus, c_m, decreases gradually. Although the concentration of sample (a), 0.25%, is actually above the CMC, c_m decreases below the CMC soon after the beginning of ultracentrifugation with this solution.

[21] H. Fujita, H. Inagaki, T. Kotake and H. Utiyama, *J. Phys. Chem.*, **66**, 4 (1962).

[22] R. J. Goldberg, *J. Phys. Chem.*, **57**, 194 (1953).

[23] J. W. Williams, K. E. Van Holde, R. L. Baldwin and H. Fujita, *Chem. Revs.*, **58**, 715 (1958).

[24] J. M. Creeth, *J. Phys. Chem.*, **66**, 1228 (1962).

TABLE III. MICELLAR MOLECULAR WEIGHTS OF β-NF (M_0)

Exp. No.	Nuclear No.	Concn. of β-NF, %	Concn. of NaCl, M	Temp. °C	Micellar M. W.	No. of Association
4	1	1.00	0.00	18.0	1.46×10^2	0.50
3	1	1.00	0.10	20.0	1.80×10^2	0.81
12	2	1.00	0.10	20.7	3.42×10^2	0.72
13	3	1.00	0.10	21.3	1.43×10^2	2.00
14	4	1.00	0.10	17.9	1.33×10^3	1.86
21	5	1.00	0.10	19.6	2.90×10^3	2.42
16	6	1.00	0.10	20.1	2.91×10^3	2.02
17	7	1.00	0.10	19.4	4.67×10^3	2.73
18	8	1.00	0.10	21.2	5.40×10^3	2.80
5	9.5	1.00	0.10	16.6	7.00×10^3	3.06
2	13.5	1.00	0.00	22.5	4.30×10^3	1.32
20	13.5	0.25	0.10	19.3	3.18×10^4	9.76
19	13.5	0.50	0.10	22.4	2.48×10^4	7.31
1	13.5	1.00	0.10	23.4	2.25×10^4	7.13

5 and the experimental results is due to the incomplete dissociation of the electrolyte.

As has been described in the experimental part, it has been assumed that the difference between the refractive indices and the partial specific volumes does not depend on SDS concentration within the range of the experimental conditions. However, these values of free ions differ slightly from those of the micelle formed above the CMC.[25,26] Though it is difficult to explain the abnormally high association observed, it might be due to the incomplete dissociation of counter ions, accompanied by the change of the equilibrium between the micelle and the free ion of SDS at a given instant of centrifugation.

The Micellar Molecular Weight of Condensates of Sodium β-Naphthalene Sulfonate.—The association of purified β-NF in water has never been studied quantitatively. It is expected that the association would occur since their molecular structure is similar to that of direct dyes.[27] In fact, at concentrations above ca. 0.015%, the association of these compounds is shown in the light of their ultraviolet spectra[28]. The Archibald method in a cylindrical lens-Schlieren optical system is not easily applicable to such low concentration regions, and its use introduces appreciable errors. Table III summerizes the molecular weights, M_0, obtained for 0.25~1.0% β-NF solutions in 0.1 M sodium chloride.

In the absence of an elctrolyte the number of association of β-NF with $x=1$ and 13.5 nearly agrees with the value for non-association. The dependency of M_0 on the concentration of β-NF is not significant at concentrations below 1.00% when 0.10 M sodium chloride is present.

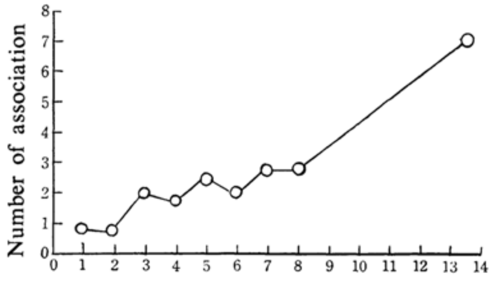

Fig. 5. Relation of number of association to x of 1.00% β-NF in 0.1 M NaCl.

Figure 5 shows that the number of association of β-NF in its 1.0% solution dissolved in 0.1 M sodium chloride increases with the number of nuclei, x, suggesting that the intermolecular van der Waals attraction[29,30] becomes stronger as x increases. The slopes of the curves of $M_m(t)$ against time for β-NF were found always to be negative. This indicates that polydispersity is more predominant than nonideality in this case. This is reversed in the case of a SDS solution more concentrated than the CMC

Summary

(1) The values of the micellar molecular weight of SDS in water and in a sodium chloride solution could not be obtained by

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[25] H. B. Klevens, *J. Phys. and Colloid Chem.*, **52**, 130 (1948).

[26] W. D. Harkins, R. W. Mattoon and M. L. Corrin, *J. Colloid Sci.*, **1**, 105 (1946).

[27] I. Vickerstaff, "The Physical Chemistry of Dyeing," London and Edinburgh, Oliver and Boyd, 2. ed., (1954).

[28] K. Hattori and Y. Tanino. *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 65 (1963).

[29] R. H. Peters and H. H. Sumner, *J. Soc. Dye. Colourists*, **71**, 130 (1955).

[30] C. H. Giles and A. S. A. Hassen, ibid., **74**, 846 (1958).

the Archibald method, whereas the observed M_0 may represent the relative values, each corresponding to a given instant of centrifugation. However, a CMC could be definitely determined which agreed with the values reported by other workers. As may be noted from the slope of the dependency of M_0 on time, the SDS solution is non-ideal above the CMC while it is polydisperse below the CMC. The abnormally high association in the critical micelle region might be caused by the incomplete dissociation of counter ions, accompanied by a change in the equilibrium between the micelle and the free ion of SDS at a given instant of centrifugation.

(2) When the electrolyte is absent, β-NF's presumably exist in a monomeric state, but in a 0.1 M sodium chloride solution they associate, the degree of association being proportional to the x. In the region of 0.25∼1.0% concentration, micelles of β-NF were observed to be polydisperse.

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