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ζ-Potentials of Natural and Synthetic Fibers in SDS Solutions and the Viscosity of SDS Solutions above the Critical Micelle Concentration[*1, *2]

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In order to investigate the adsorption behavior of an anionic surfactant on fibers, the ζ-potentials of natural and synthetic fibers in aqueous solutions of sodium dodecyl sulfate (SDS), mainly above the critical micelle concentration (CMC), were measured. Further, the change in the structure of the SDS micelle in aqueous solutions was studied by means of the viscosity method. At first the reduced viscosity for the SDS micelle, η_{spm}/c_m (c_m: the micellar concentration), increased rapidly with the c_m as long as the c_m was small; thereafter, after a break, it approximated the saturated values as a whole. The results calculated from the experimental data using Jones and Dole's equation showed two distinct breaks. The first break corresponded to the 1st CMC, and the second, nearly to the break in the η_{spm}/c_m *vs.* c_m curve. In addition, the intrinsic viscosity for the SDS micelle, $[\eta]_M$, and the effective specific volume, V, were obtained. From these results, it can be assumed that the structure of the SDS micelle is variable at the break in the η_{spm}/c_m *vs.* c_m curve. The ζ-potentials of fibers in aqueous SDS solutions changed rapidly with an increase in the concentration of SDS, but they remained approximately constant in the vicinity of the CMC. At much higher concentrations above the CMC (in the vicinity of the SDS concentration of 2×10^{-2} mol/l), the ζ values again gradually changed; thereafter, after a break, they became nearly constant again. The change in the ζ-potentials corresponds approximately to the break in the η_{spm}/c_m *vs.* c_m curve. Therefore, it may be suggested that it is connected with the change in the structure of the SDS micelle.

The adsorption of an anionic surface active agent on the fiber-solution interfaces is considered to be an important factor in problems of detergency. It is generally known that the washing power of a surfactant increases up to a certain concentration of surfactant; beyond this point, however, the further addition of the surfactant has little effect.[1-3)]

On the other hand, in the case of the adsorption of a surfactant on solid materials, the appearance of maxima in adsorption isotherms has been observed by many authors.[4-11)] It seems that the maxima in adsorption isotherms correspond to the critical washing concentration (CWC) in detergency. However, several investigators[12-17)] did not clearly observe such maxima in isotherms.

Previous papers[18)] have described the relationship

[*1] This paper is Part VIII in a series on "Surface Adsorption Properties and ζ-Potentials of Fibrous Materials in Surface Active Agent Solutions"; Part VII: T. Suzawa and M. Yuzawa, *Yukagaku*, **15**, 20 (1966).

[*2] Presented at the 21st Symposium of Colloid and Interface Chemistry, Kyoto, Nov. 2, 1968; at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April 7, 1969, and at the Meeting of Oil Chemistry of the Japan Oil Chemists' Society, Osaka, Nov. 6, 1969.

1) W. C. Preston, *J. Phys. & Colloid Chem.*, **52**, 84 (1948).

2) E. K. Goette, *J. Colloid Sci.*, **4**, 459 (1949).

3) T. Tachibana, A. Yabe and M. Tsubomura, *ibid.*, **15**, 278 (1960).

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5) A. L. Meader and B. A. Fries, *Ind. Eng. Chem.*, **44**, 1636 (1952).

6) R.D. Vold and A.K. Phansalkar, *Rec. Trav. Chim. Pays-Bas*, **74**, 41 (1955).

7) A. Fava and H. Eyring, *J. Phys. Chem.*, **60**, 890 (1956).

8) R. D. Vold and N. H. Sivaramakrishnan, *ibid.*, **62**, 984 (1958).

9) H. C. Evans, *J. Colloid Sci.*, **13**, 537 (1958).

10) H. J. White, Y. Gotshal, L. Robenfeld and F. H. Sexsmith, *ibid.*, **14**, 598 (1959).

11) F. Z. Saleeb and J. A. Kitchener, *J. Chem. Soc.*, **1965**, 911.

12) A. S. Weatherburn and C. H. Bayley, *Textile Res. J.*, **22**, 797 (1952).

13) M. Hayashi and Y. Nakazawa, *Radioisotopes*, **8**, 149 (1959).

14) M. Hayashi, This Bulletin, **33**, 1184 (1960).

15) C. Sakai and S. Komori, *Yukagaku*, **14**, 66 (1965).

16) J. A. Kitchener, *J. Phot. Sci.*, **13**, 152 (1965).

17) B. E. Gordon, G. A. Gillies, W. T. Shebs, G. M. Hartwig and G. R. Edwards, *J. Amer. Oil Chem. Soc.*, **43**, 232 (1966).

18) a) T. Suzawa, *Kogyo Kagaku Zasshi*, **66**, 1002 (1963). b) T. Suzawa and M. Yuzawa, *Yukagaku*, **15**, 20 (1966).

between the ζ-potentials of synthetic fibers in aqueous solutions of a surfactant and the surface-adsorption properties of its agent on the fibers below the critical micelle concentration (CMC). It was suggested that the adsorption of an anionic surfactant on fibers in an aqueous neutral solution takes place mainly by means of van der Waals' force. Further, the amount of anionic surfactant adosorbed per unit of the area of the fiber surface increased with an increase in the concentration of its agent; the increase was the greater, the smaller the degree of swelling of the fiber and the more hydrophobic the fiber. These facts indicate that the interaction between the hydrocarbon chain of an anionic surfactant and the hydrophobic part of a fiber is important for the adsorption of its agent on the fiber.

At present, in order to contribute to the study of the adsorption behavior of an anionic surfactant on the fibers in the vicinity of the CMC and above of its agent, the ζ-potentials of natural and synthetic fibers in aqueous solutions of sodium dodecyl sulfate (SDS) were measured. On the other hand, the viscosity of an aqueous SDS solution was determined in order to investigate the relationship between the structure of the micelle and the concentration of the surfactant. In this paper, the relationship between the ζ-potentials of fibers in aqueous solutions of SDS and the change in the structure of the SDS micelle will be primarily reported on.

Experimental

Apparatus and Procedures. *ζ-Potential.* The ζ-potential was measured by the method of the streaming potential described in a previous paper.[19] The streaming potential was measured by using a Transistorized Dynamic-Condenser Electrometer, Model UFE 26301 H (Tokyo Shibaura Electric Co., Ltd.). The relation between the streaming potential, H (mV), and the pressure, P (cmHg), is shown in Figs. 1 and 2, the figures corresponding, respectively, to Nylon 6 and Cashimilon fibers. On the basis of these results, the streaming potential can be said to be accurately proportional to the pressure (*i. e.*, to the velocity of streaming) between mercury pressures of 3 and 6 cm above the CMC as well as below it.

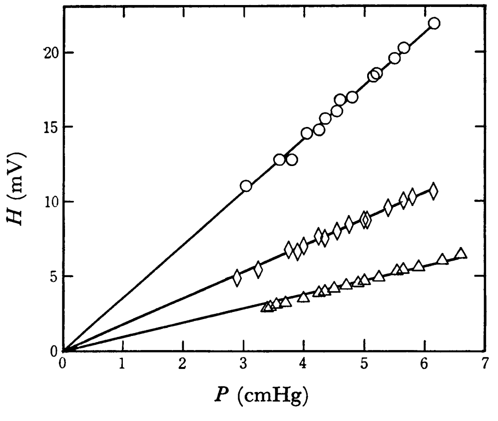

Fig. 1. Relation of streaming potential (H) to pressure (P) for Nylon 6 fiber.
SDS concentration (mol/l):
(○) 4×10^{-3}; (◇) 10×10^{-3}; (△) 26×10^{-3}

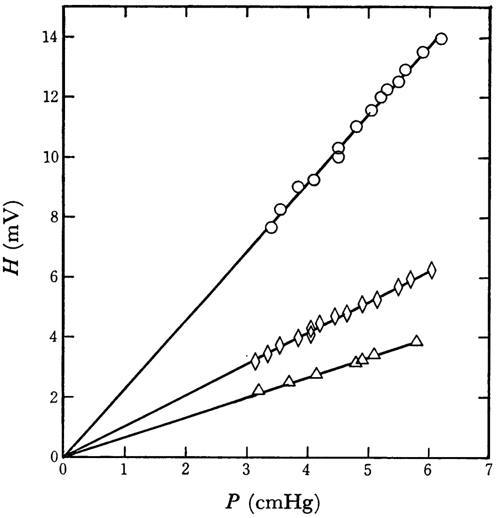

Fig. 2. Relation of streaming potential (H) to pressure (P) for Cashimilon fiber.
SDS concentration (mol/l):
(○) 4×10^{-3}; (◇) 10×10^{-3}; (△) 26×10^{-3}

Actually, the streaming potential measurements were always carried out at a mercury pressure of 5 cm and at a temperature of 25±0.02°C. The solutions examined all contained 10^{-4} mol/l of sodium chloride.

Critical Micelle Concentration (CMC). The critical micelle concentration was determined by measuring the surface tension, the conductance, and the viscosity of aqueous solutions of the surfactant in the presence of 10^{-4} mol/l sodium chloride and at 25±0.02°C.

Surface Tension: A drop method was used for measuring the surface tension of solutions. The surface-tension values were corrected by the method of Harkins and Brown.[20]

Conductance: The conductance values were obtained by means of a Yanagimoto Conductivity Outfit, Model MY-7 (Yanagimoto MFG. Co., Ltd.).

Viscosity: The viscosities of the solutions were measured with an Ostwald viscometer prepared by reference to the British Standard,[21] so the surface tension correction was small.[22] The capillary of this viscometer was 12.5 cm long, and its average radius was 0.028 cm. Reynolds number was about 30. The kinetic correction amounted to less than 1 part in 1000 over the whole concentration range studied.[22]

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[19] T. Suzawa, T. Saito and H. Shinohara, This Bulletin, **40**, 1596 (1967).

[20] W. D. Harkins and F. E. Brown, *J. Amer. Chem. Soc.*, **38**, 288 (1916); *ibid.*, **41**, 499 (1919).

[21] A. E. Alexander and P. Johnson, "Colloid Science," Appendix IV (1949).

[22] Y. Iwadare and T. Suzawa, *Nippon Kagaku Zasshi*, **90**, 1106 (1969).

The viscometer was cleaned immediately before each filling with a warm sulfuric acid-dichromate solution, rinsed numerous times in order to remove all traces of the acid, and dried with air. The flow time for water was 663.9 sec. From three to five flow-time measurements were made on each solution.

Materials. *Fibers.* Polyamide Nylon 6 (manufactured by the Toray Co., Ltd.; draw ratio, 1; denier, unknown; 30 filaments), polyvinylalcohol Vinylon (Kurashiki Rayon Co., Ltd.; 1.4 denier; monofilament; degree of formylation, 0.34), polyacrylonitrile Cashimilon (Asahi Chemical Industry Co., Ltd.; 52 counts; monofilament) and polypropylene Pylen (Toray Co., Ltd.; 100 denier; 24 filaments) were first extracted with ethanol for about 24 hr at room temperature; then they were extracted with deionized water and finally dried in air. Cotton fiber (Kanegafuchi Spinning Co., Ltd.; 30 counts; yarn) was extracted with deionized water, with ethanol, and with an ethanol-benzene mixed solvent (volume ratio 1: 1) for 24 hr at room temperature; finally it was extracted with deionized water.

Glass capillaries were used instead of glass fiber. Hario glass tubes (JIS K-250) sold by the Shibata Chemical Apparatus Mfg. Co., Ltd., were used for the capillaries. These capillaries were 23 mm long, and their average inner and outer diameters were 0.2 and 0.4 mm respectively. They were cleaned with a warm sulfuric acid - dichromate solution and rinsed numerous times with conductivity water in order to remove all traces of acid by means of suction with a aspirator.

Surface Active Agent. The sodium dodecyl sulfate (SDS) was provided by the Nippon Oils & Fats Co., Ltd. The surface tension *vs.* the log concentration curve showed no minimum. The CMC values obtained are given in Table 1.

TABLE 1. THE CMC VALUES OF SDS IN AQUEOUS SOLUTION (NaCl: 10^{-4} mol/l, 25°C)

Method	CMC (mol/l) $\times 10^3$
Surface tension	7.1
Conductivity	7.6
Viscosimetry	7.0

Results and Discussion

Viscosity of SDS Solution and Change in the Structure of SDS Micelles. *Viscosity of Aqueous SDS Solution.* The results of the viscosity measurement for an aqueous SDS solution in the presence of 10^{-4} mol/l sodium chloride are shown in Fig. 3. The SDS solution was studied over the concentration range $(4—255) \times 10^{-3}$ mol/l.

The variation in the relative viscosity, η_r, with the SDS concentration, c_s (mol/l), is shown by curve I. The gentle upward curvature of the curve seems to be a result of mutual interference between the colloidal particles in motion during flow.[23]

The relation between the reduced viscosity, η_{sp}/c_s, and c_s, as is shown by curve II, reaches a minimum at the SDS concentration of 7×10^{-3} mol/l. This minimum point is believed to correspond to the CMC, $c_{c(1)}$, it agrees well with the CMC value obtained by surface-tension measurements (*cf.* Table 1).

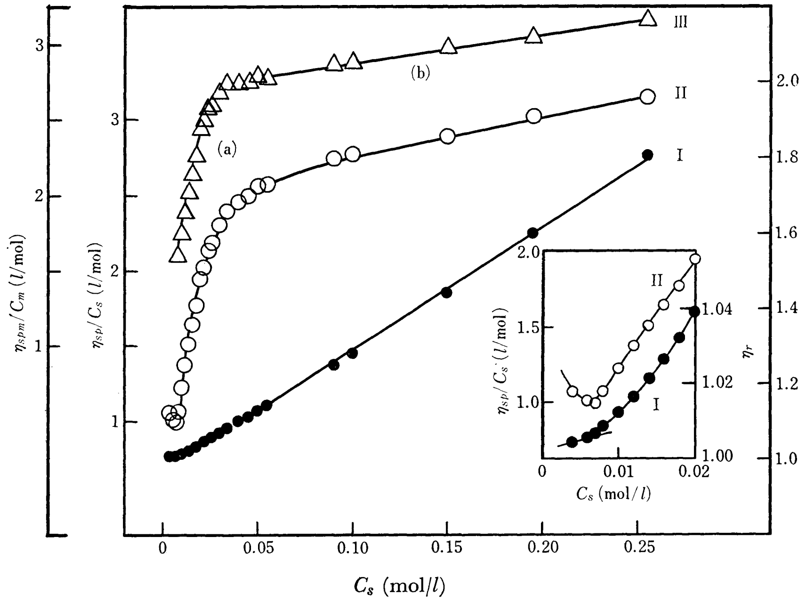

Fig. 3. Viscosity of aqueous SDS solution.
curve I: η_r *vs.* c_s; curve II: η_{sp}/c_s *vs.* c_s; curve III: η_{spm}/c_m *vs.* c_m

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[23] R. J. Vetter, *J. Phys. & Colloid Chem.*, **51**, 262 (1947).

Sata and Tyuzyo[24] presumed that above the 1st CMC, the concentration of a surfactant monomer in a solution which is in equilibrium with the micelle is almost constant and remains unchanged. Accordingly, the following operations were performed:

$$c_m = c_s - c_{c(1)}$$

$$\eta_{spm}/c_m = \{(\eta_r/\eta_{rc(1)}) - 1\}/(c_s - c_{c(1)}) \qquad (1)$$

where;

η_{spm}/c_m: reduced viscosity for the micelle.

$\eta_{rc(1)}$: relative viscosity at the 1st CMC, $c_{c(1)}$.

Therefore, the recuced viscosity for SDS micelles, η_{spm}/c_m, is shown by curve III.

From this figure, it can be seen that the η_{spm}/c_m increases linearly with the c_m as long as the c_m is small; thereafter, after a break observed in the concentration range $(20\text{—}25) \times 10^{-3}$ mol/l, it approximates the saturated value as a whole. The second, sharper break did not appear in the concentration range studied.

Intrinsic Viscosity and Hydration of SDS Micelles. Shinoda[25] has suggested that the shape and the size of micelle depend on the concentration, the temperature, the molecular structure of the respective surface active agent, the kind of intermolecular force, and the kinds of additives. Grindley and Bury[23,26] have indicated that the micelle size increases to a maximum over a short transition concentration range. At present, while the evidence that amphipathic molecules associate to form aggregates of micelles is overwhelming, the size and shape of these micelles are still disputed.[27]

Mukerjee[28] has estimated the hydrations of micelles of SDS and dodecyl and tetradecyl trimethyl ammonium chlorides from the viscosity data in the following manner. That is, the hydration, h, in weight percentage is obtained, assuming that the micelles are spherical, from an extension of Einstein's equation:

$$[\eta]_M = 2.5(\bar{V}_s' + h) \qquad (2)$$

where $[\eta]_M$ is the corrected intrinsic viscosity for the charged micelle, and where $\bar{V}_s'$ is the partial specific volume of the micelle. Consequently, it was concluded that the formation of ice-like hydration sheaths on hydrocarbon surfaces and the thickening of the shear layer on highly-charged surfaces because of the viscoelectric effect are probably unimportant.

Table 2. Intrinsic viscosities and hydration of SDS micelles

	$[\eta]_M$ (ml/g)	Hydration in weight per cent		Hydrodynamic volume	Hydration in volume per cent
		Author	Mukerjee[28]		
Portion (a)	3.3	43	39±4	1.32	24
Portion (b)	7.5	211		3.00	67

On the basis of Eq. (2), the hydration of SDS micelles obtained from the curve III are shown in Table 2. Further, in the table the hydrodynamic volumes[23] and hydrations in volume percentage, calculated from hydrodynamic volumes, are also shown. The electroviscous effect, included as part of the intrinsic viscosity, was corrected for by using the data of Parker and Wasik.[29] The partial specific volume of SDS micelles, $\bar{V}_s'$, is 0.889 ml/g.[30]

At all events, on the basis of Table 2 it seems likely that the degree of hydration and, hence, the size of SDS micelles increase to some extent with an increase in the concentration on the portion (a). As the solution becomes more concentrated, the counter-ion concentration steadily increases, with a resulting decrease in the degree of ionization of the micelles; the stability is thereby enhanced.[31] The reduced viscosity for SDS micelles, η_{spm}/c_m, linearly increases little by little with an increase in the concentration on the portion (b). This fact suggests that the micellar properties remain constant over a relatively wide range of concentration, indicating that the dimensions and the form of the micelles remain constant.[32,33]

Effective Specific Volume of SDS. Use was made of Guth and Simha's equation,[32,34,35] which is a form of Einstein's equation extended for application to more concentrated solutions:

$$\eta_r = 1 + 2.5\phi + 14.1\phi^2 \qquad (3)$$

where ϕ is the volume fraction occupied by the spherical particles. The effective specific volume of 1 g of a surfactant including hydrated water, V, is expressed as follows[32,35]:

$$V = \phi/c \qquad (4)$$

where c is the concentration of the solution in g/ml.

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24) N. Sata and K. Tyuzyo, This Bulletin, **26**, 177 (1953).

25) K. Shinoda, T. Nakagawa, B. Tamamushi and I. Isemura, "Colloidal Surfactants," Academic Press Inc., New York (1963), p. 25.

26) J. Grindley and C. R. Bury, *J. Chem. Soc.*, **1929**, 679.

27) L. I. Osipow, "Surface Chemistry," Reinhold Publishing Corporation, New York (1963), p. 174.

28) P. Mukerjee, *J. Colloid Sci.*, **19**, 722 (1964).

29) R. A. Parker and S. P. Wasik, *J. Phys. Chem.*, **62**, 967 (1958).

30) P. Mukerjee, *ibid.*, **66**, 1733 (1962).

31) K. A. Wright and H. V. Tartar, *J. Amer. Chem. Soc.*, **61**, 544 (1939).

32) D. C. Robins and I. L. Thomas, *J. Colloid Interfac. Sci.*, **26**, 415 (1968).

33) T. Ito and H. Mizutani, *Yakugaku*, **17**, 246 (1968).

34) E. Guth and R. Simha, *Kolloid-Z.*, **74**, 266 (1936).

35) K. Shinoda, T. Nakagawa, B. Tamamushi and T. Isemura, "Colloidal Surfactants," Academic Press Inc., New York (1963), p. 115.

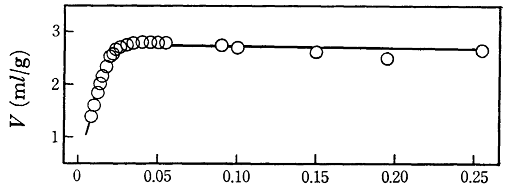

Fig. 4. Effective specific volume (V) with SDS concentration.

The values of V thus calculated are shown in Fig. 4. The effective specific volume of the dispersed colloidal particles of SDS increases with the concentration as long as the SDS concentration is small; thereafter, after a break, it remains approximately constant in the range of high concentration. This break roughly corresponds to that of curve III in Fig. 3. The constancy of the effective specific volumes is also indicative of a spherical micelle.[32,35] Therefore, the shape and size of these micelles must remain constant in the range of concentration beyond the break, but they are not constant in the smaller range.

The Change in the Structure of SDS Micelle Observed from Jones and Dole's Equation. The relative viscosity of an electrolyte solution with a molar concentration, m, is given by Jones and Dole's equation[28,36,37]:

$$\eta_r = 1 + A\sqrt{m} + Bm \qquad (5)$$

where A and B are constants. It is believed that the B coefficient for a particle in water is a positive quantity indicating a structure-forming tendency. On the other hand, if the electrolyte particle tended to destroy the structure of water and produce disorder, then the B coefficient would be a negative quantity.[37]

It is suggested that the formation of micelles is attended by a change in the structure of the solvent, that is, by an interaction between micelles and solvent.[23] If the change in the structure of the micelle were attended by a change in the structure of water, the B coefficient would be variable.

The results calculated from the experimental data are shown in Fig. 5. From this figure, it can be seen that there are two distinct breaks, at points a and b. The point a nearly corresponds to the 1st CMC, and the point b, roughly to the break of curve III in Fig. 3 and to that of the V *vs.* concentration curve in Fig. 4.

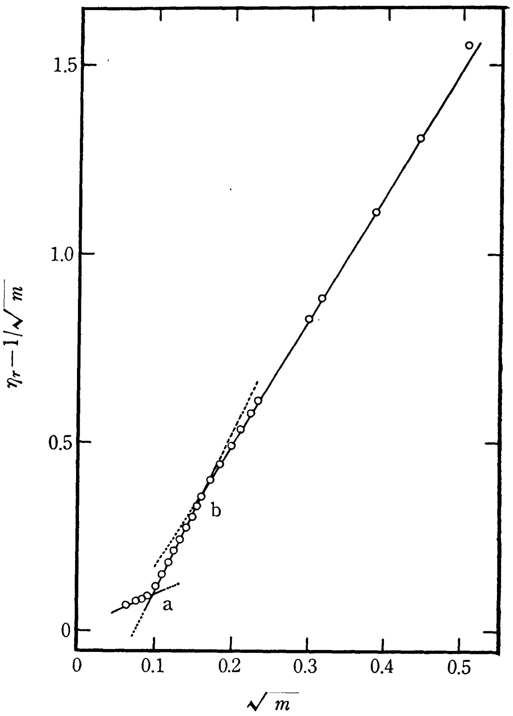

Fig. 5. Behaviour in viscosity of aqueous SDS solution observed by Jones and Dole's equation.

Nakagaki and Ninomiya[38] have shown the viscosity data that the 2nd CMC of SDS is 0.02 mol/l (40°C). This concentration nearly corresponds to that of the point b in the curve. On the basis of these results, it can be assumed that the structure of the SDS micelle is variable at the point b in Fig. 5.

ζ-Potential of Fibers in Aqueous SDS Solutions. *ζ-Potential below the CMC.* The ζ-potential was measured over the SDS concentration range $(0-30)\times 10^{-3}$ mol/l in the presence of 10^{-4} mol/l sodium chloride, and every hour on the hour. The results obtained are shown in Fig. 6. These are the equilibrium values which were approximated after four hours of immersion.

The ζ-potential for the Nylon 6 fiber is negative and rapidly increases with an increase in the SDS concentration. This fact suggests that, in spite of the negative charge of Nylon 6 in an aqueous solution, the amount of SDS adsorbed on the surface of the fiber rapidly increases with an increase in the agent concentration. It can also be suggested that the Nylon 6 fiber combines mainly with SDS by means of van der Waals' force, as has been described in a previous paper.[18b)]

The ζ *vs.* SDS concentration curve for the Pylen fiber resembles that for Nylon 6 very closely in its behavior, but the negative ζ values for the former are larger than those for the latter over the concentration range studied. This fact suggests that surface-surfactant adsorption for the Pylen fiber is appreciably larger than that for the Nylon 6 fiber.[18b)]

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36) G. Jones and M. Dole, *J. Amer. Chem. Soc.*, **51**, 2950 (1929).

37) M. Abu-Hamdiyyah, *J. Phys. Chem.*, **69**, 2720 (1965).

38) M. Nakagaki and Y. Ninomiya, This Bulletin, **37**, 817 (1964).

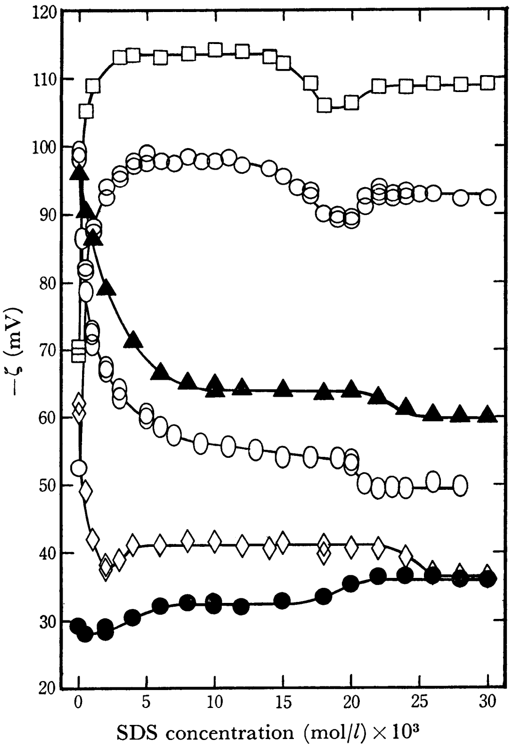

Fig. 6. ζ-potentials for fibers with SDS concentration.

(□) Pylen; (○) Nylon 6; (▲) Cashimilon; (0) glass; (◇) Vinylon; (●) cotton

On the other hand, the ζ-potentials for the glass and Cashimilon rapidly decrease with an increase in the SDS concentration. It can be suggested that the decrease in ζ values with an increase in the concentration may be due to a decrease in the thickness of the double layer, because the total ionic strength in solutions increases with an increase in the concentration. Furthermore, it may be due to a small adsorption of SDS on the surfaces of these samples, because of the large electrostatic repulsion between the surfaces of fibers and SDS anions.

A similar behavior for the ζ *vs.* SDS concen tration curve of Vinylon is also observed, except that this curve passes through a minimum at the 2×10^{-3} mol/*l* concentration. It is not at all clear why the ζ-potential of Vinylon shows its minimum at this concentration.

The negative ζ-potential for cotton increases from about 29 mV at the SDS concentration of zero to about 32 mV at the CMC. This change in the ζ-potential is small; therefore, it can be presumed that the surface-surfactant adsorption for cotton is small, in spite of the small electrostatic repulsion between the surfaces of the fiber and the SDS anions.

ζ-Potential in the Vicinity of the CMC. The ζ-potentials of all the fibers investigated remain nearly constant in the vicinity of the CMC. This constancy is also kept to some distance above the CMC. On the basis of these results, it can be presumed that the surface adsorption of SDS on fibers remains nearly constant in this concentration range.

Relationship between the Change in ζ-Potentials of Fibers and That in the Structure of the SDS Micelle. As the solution becomes more concentrated, the ζ-potentials for fibers change again; thereafter, after a minimum or a break, they again remain constant. It is rather interesting that the ranges of SDS concentration in which the apparent changes of the ζ-potentials of fibers are observed correspond approximately to the concentration for the break in curve III in Fig. 3, to that for the break in the curve in Fig. 4, and to that for the point b in Fig. 5.

From these facts, it can be presumed that, if the structure of the micelle changed at the concentration for the break in the η_{spm}/c_m *vs.* c_m curve, as has been mentioned above, there would be a change in the structure of the diffuse double layer and that, consequently, the ζ-potentials of the fibers would change.

In more concentrated solutions, the degree of ionization of the micelle must be more decreased and the stability thereby enhanced.[31] As is shown by the viscosity data (*cf.* Table 2 and Figs. 3—5), the micellar properties remain constant over a relatively wide range of concentrations, indicating that the size and the shape of micelle remain approximately constant.[32,33] Consequently, the structure of the double layer should again be kept stable. It is, therefore, understandable that the ζ-potentials for fibers are again kept constant in much higher concentration ranges, that is, in $(22—30)\times10^{-3}$ mol/*l* for Pylen, Nylon 6, and cotton, in $(25—30)\times10^{-3}$ mol/*l* for Cashimilon and Vinylon, and in $(21—28)\times10^{-3}$ mol/*l* for glass.

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