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ζ-Potentials of Synthetic Fibers in Aqueous Solutions of Sodium Alkyl Sulfates and Viscosities of Their Solutions[*1,*2]

Yoshio IWADARE

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Senda-machi, Hiroshima

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In order to study the surface-adsorption behavior of anionic surfactants on fibers, the ζ-potentials of some synthetic fibers in aqueous solutions of sodium alkyl sulfates and their mixtures mainly above the critical micelle concentration (CMC), were measured. Further, the viscosities of aqueous solutions of pure surfactants were determined. Consequently, it can be presumed, on the basis of the viscosity data, that the structure of the micelles of these agents varies at the break of the η_{spm}/c_m *vs.* c_m curve. The ζ-potentials (negative) of fibers in aqueous solutions of the agents rapidly changed with an increase in the agent concentrations, but it remained nearly constant above the CMC. At much higher concentrations, the ζ values gradually changed; thereafter, passing a break or a minimum, they became approximately constant again. The concentration at the break or the minimum observed nearly corresponded to that at the break of the η_{spm}/c_m *vs.* c_m curve. It may, therefore, be suggested that the change in ζ-potentials at high concentrations is connected with that in the structure of the micelles. The ζ-potentials (negative) of fibers in aqueous mixed solutions changed sharply with an increase in the concentration of the mixtures and thereafter, passing a maximum in the vicinity of the CMC, complicatedly changed as the total concentrations and mixing ratios changed.

The determination of the adsorption behavior of surfactants on solid surfaces, especially on fiber surfaces, is of fundamental importance in a study of the mechanism of the detergent action. A few investigators[1-4] previously attempted to elucidate the adsorption behavior of surfactants on fiber surfaces, mainly below the critical micelle concentration (CMC), by measuring the ζ-potential of the fiber-solution interface, but little work was done in systems above the CMC.[1,2]

The present author has, therefore, tried to make clear the adsorption behavior of anionic surfactnats on the surfaces of several fibers, mainly near and above the CMC. In a previous experiment,[5] in order to ascertain the surface-adsorption properties of sodium dodecyl sulfate (SDS) on fibers, the ζ-potentials of natural and synthetic fibers in aqueous solutions of the agent were measured, and then the amounts of SDS adsorbed per unit of area of the fiber surfaces were calculated from the ζ values thus obtained. In another investigation,[6] the viscosities of aqueous solutions of SDS and sodium tetradecyl sulfate (STS) were determined as part of a study of the structure of the micelles of these agents. Further, the relation between the change in the ζ-potentials of fibers and that in the structure of SDS micelle was discussed in detail.[7]

In this investigation, in order to clarify the structure of micelles of aqueous sodium alkyl sulfates, the viscosities of aqueous solutions of sodium hexadecyl sulfate (SHS) were determined in a manner similar to that mentioned previously.[6] The ζ-potentials of some synthetic fibers in aqueous of the pure surfactants were measured, and then the relation between the change in the ζ-potentials of these fibers and that in the structure of the surfactant micelles was discussed. In addition, the ζ-potentials of fibers in aqueous solutions of

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[*1] This paper is Part X in a series on "Surface Adsorption Properties and ζ-Potentials of Fibrous Materials in Surfactant Solutions," Part IX: Y. Iwadare, M. Sasaki and T. Suzawa, *Kogyo Kagaku Zasshi*, **73**, 1927 (1970).

[*2] Presented at the 21st Symposium on Colloid and Interface Chemistry, Kyoto, Nov. 2, 1968; at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April 7, 1969; at the Meeting on Oil Chemistry of Japan Oil Chemists' Society, Osaka, Nov. 6, 1969, and at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April 5, 1970.

1) J. S. Stanley, *J. Phys. Chem.*, **58**, 533 (1954).

2) M. v. Stackelberg, W. Kling, W. Benzel and F. Wilke, *Kolloid-Z.*, **135**, 67 (1954).

3) T. Suzawa, *Kogyo Kagaku Zasshi*, **65**, 2042 (1962).

4) T. Suzawa, *ibid.*, **66**, 1002 (1963).

5) Y. Iwadare, M. Sasaki and T. Suzawa, *ibid.*, **73**, 1927 (1970).

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

7) Y. Iwadare and T. Suzawa, This Bulletin, **43**, 2326 (1970).

mixtures of the two surfactants (that is, SDS-STS and STS-SHS mixtures) were measured and compared with those obtained in pure surfactant solutions.

Experimental

Apparatus and Procedures. *ζ-Potential.* The ζ-potential was determined by the method of the streaming potential, which has been described previously.[5,8] The streaming potential was measured by using a Transistorized Dynamic-Condenser Electrometer, Model UFE 26301 H (Tokyo Shibaura Electric Co., Ltd.). The conductance of the solutions was obtained from a Yanagimoto Conductivity Outfit, Model MY-7 (Yanagimoto MFG. Co., Ltd.).

The streaming potential was accurately proportional to the pressure in the range from 30 to 60 mmHg above the CMC, as well as below it,[7] regardless of the kinds of the fibers, the kinds, mixing ratios and concentrations of the surfactants, and the temperatures. Actually, the streaming potential measurements were carried out at 50 mmHg and at 25±0.02°C for SDS and the SDS-STS mixture, at 40±0.02°C for STS, and at 45±0.02°C for SHS and the STS-SHS mixture. The solutions examined contained 10^{-4} mol/*l* of sodium chloride.

Viscosity. Viscosity measurements were made with an Ostwald viscometer, as has been described in a previous paper.[6] The flow time for the water was 448.2 sec at 45±0.02°C. The Reynolds' number was about 65. The kinetic energy correction was less than 1 part in 1000 over the whole concentration range investigated. From three to five flow-time measurements were made on each solution. The solution 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 surfactant solutions in the presence of 10^{-4} mol/*l* of sodium chloride, as has been described previously.[7]

Materials. *Fibers.* The polypropylene Pylen, polyamide Nylon 6, polyacrylonitrile Cashimilon, and polyvinyl alcohol Vinylon fibers were the same as those used in previous works.[5,7]

Surface Active Agents. The sodium dodecyl (SDS) and tetradecyl (STS) sulfate used were the same as in a previous study.[6] The sodium hexadecyl sulfate (SHS) was prepared from hexadecyl alcohol which contained 0.6% C_{14} and 1.2% C_{18} alcohols as impurities.

Table 1. The CMC of sodium alkyl sulfates of 10^{-4} mol/*l* of sodium chloride

Surfactants	CMC (mol/*l*)×10^3		
	Surface tension	Conductivity	Viscosimetry
SDS (25°C)	7.1	7.61	7.0
STS (40°C)	2.13	2.20	2.0
SHS (45°C)	0.61	0.71	0.6

This substance was twice recrystallized from ethanol and then carefully extracted with petroleum ether for 50 hr in order to remove unreacted alcohol. The purified substance had a purity of at least 99.85%; most of the impurity was moisture. The surface tension *vs.* log concentration curve was free of a minimum. The CMC values obtained are given in Table 1.

Results and Discussion

Viscosities and Structure of Micelles of Aqueous Sodium Alkyl Sulfates

Viscosities of SDS and STS Solutions and Change in the Structure of SDS and STS Micelles. The viscosities of aqueous SDS and STS solutions were reported in a previous paper.[6] The reduced viscosities for the micelles of these agents, η_{spm}/c_m (c_m: the micellar concentration),*3 increased rapidly with the c_m as long as the c_m was small; thereafter, passing a break, they gradually increased with the increase in c_m. The break was observed in the (20—25)×10^{-3} mol/*l* concentration range for SDS and at (8—10)×10^{-3} mol/*l* for STS. The intrinsic viscosity,[11] the hydration,[11,12] and the hydrodynamic volume[12] for the micelle observed in the higher concentration range, above the break, were much larger than those of the lower concentration range, below it.

From Guth and Simha's equation,[13-15] the effective specific volumes,[14,15] of these agents including hydrated water were calculated. They increased with the agent concentrations, but thereafter, passing a break, remained nearly constant. The break nearly corresponded to that of

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

*3 As has been shown in previous papers, the following operations were performed[9,10]

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

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

where;

c_s: surfactant concentration.

$c_{c(1)}$: the 1st CMC.

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

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

9) N. Sata and K. Tyuzyo, *ibid.*, **26**, 177 (1953); H. Okuyama and K. Tyuzyo, *ibid.*, **27**, 259 (1954); K. Tyuzyo, *ibid.*, **31**, 117 (1958); K. Tyuzyo, *Kolloid-Z.*, **175**, 40 (1961).

10) N. Nakagaki and Y. Ninomiya, This Bulletin, **37**, 817 (1964).

11) P. Mukerjee, *J. Phys. Chem.*, **66**, 1733 (1962).

12) R. J. Vetter, *J. Phys. & Colloid Chem.*, **51**, 262 (1947).

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

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

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

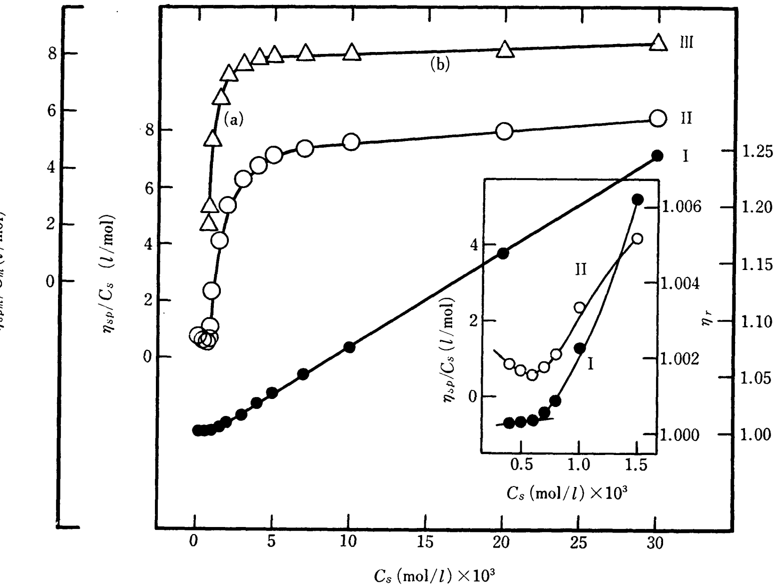

Fig. 1. Viscosity of aqueous SHS solution (45°C).
curve I: η_r *vs.* c_s, curve II: η_{sp}/c_s *vs.* c_s, curve III: η_{spm}/c_m *vs.* c_m
Inset: enlarged in the vicinity of the CMC.

the η_{spm}/c_m *vs.* c_m curve.

The results calculated from the experimental data using Jones and Dole's equation[11,16,17] showed two distinct breaks. The first break corresponded to the 1st CMC of these agents, while the second corresponded approximately to the break in the η_{spm}/c_m *vs.* c_m curve.

From these results, it may be presumed that the structures of the micelles of these surfactants in an aqueous solution would vary at the break of the η_{spm}/c_m *vs.* c_m curve.

Viscosity of SHS Solution and Change in the Structure of SHS Micelle. *i) Viscosity of Aqueous SHS Solution.* The results of viscosity measurements for an aqueous SHS solution are shown in Fig. 1. Curve I clearly breaks at the concentration of 0.6×10^{-3} mol/*l* (*cf.* inset). The gentle upward curvature with η_r above the break seems to result from mutual interference between micelles in motion during the flow.[12] Curve II shows a minimum at the break of curve I. The minimum point is believed to correspond to the CMC[9,10] and agrees well with the CMC value obtained by surface-tension measurements (*cf.* Table 1). The behavior of η_{spm}/c_m was similar to those in SDS[6] and STS[6] micelles. A break of its curve was observed in the concentration range of $(3-4)\times10^{-3}$ mol/*l*. The intrinsic viscosity of the SHS micelle obtained from the higher concentration range, above the break, was much larger than that of the lower concentration range below it.

On the other hand, Grindley and Bury[12,18] and Suzuki and Sasaki[19] have indicated that the size of the micelles increases to a maximum over a narrow transition range of concentration. From the results mentioned above, it may be presumed that the size of the SHS micelle increases to some extent with an increase in the agent 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 micelle; the stability of the micelles is thereby enhanced.[20] It can, therefore, be assumed that the micellar properties remain unchanged over a relatively wide range of concentration on the portion (b), suggesting that the size and shape of micelles remains constant.[15,21]

ii) Effective Specific Volume. Guth and Simha's equation[13-15] was used for the calculation of the effective specific volume of the surfactant, including hydrated water.[14,15] The results obtained are shown in Fig. 2. The concentration at the break in the curve corresponded well to that at

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

17) L. Gargallo, L. Sepulveda and J. Goldfarb, *Kolloid-Z. Z. Polym.*, **229**, 51 (1969).

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

19) H. Suzuki and T. Sasaki, Preprints for the 22nd Annual Meeting of the Chemical Society of Japan, separate volume 1, Tokyo (1969), p. 188.

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

21) T. Ito and H. Mizutani, *Yukagaku*, **17**, 246 (1968).

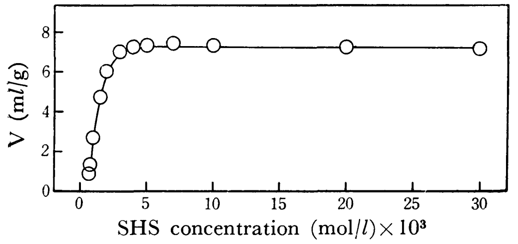

Fig. 2. Effective specific volume (V) of SHS (45°C).

the break of curve III in Fig. 1. The constancy of the effective specific volume is indicative of a spherical micelle.[14,15] Therefore, the shape and size of SHS micelle must remain unchanged in the range of concentration above the break, but is not unchanged below it.

iii) Change in the Structure of the SHS Micelle Observed from Jones and Dole's Equation. The results calculated from the experimental data using Jones and Dole's equation[11,16,17] are shown in Fig. 3. It is recognized that there are two distinct breaks, at points a and b. Point a corresponds to the 1st CMC of this agent, while point b corresponds well to the break of curve III in Fig. 1.

It is suggested that the formation of the micelle is attended by a change in the structure of the solvent, that is, by an interaction between the micelle and the solvent.[12] Therefore, if the change in the structure of micelle is attended by a change in the structure of water, the coefficient B in the equation will be variable.*4 It is noticed that the coefficient B evidently changes at point b.

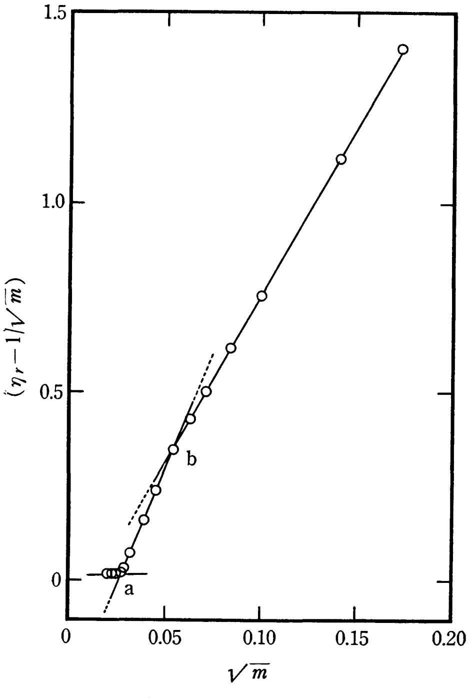

Fig. 3. Behavior of viscosity of aqueous SHS solution observed from Jones and Dole's equation (45°C).

From these results it may be presumed that the structure of the SHS micelle in an aqueous solution would change at point b in Fig. 3, that is, at the break of curve III in Fig. 1.

ζ-Potentials of Fibers in Aqueous Solutions of Pure Sodium Alkyl Sulfates

ζ-Potentials of Synthetic Fibers in an Aqueous SDS Solution. The ζ-potentials of natural and synthetic fibers in an aqueous SDS solution were reported in detail in a previous paper.[7] As an example, the ζ-potentials of four synthetic fibers are shown in Fig. 4.

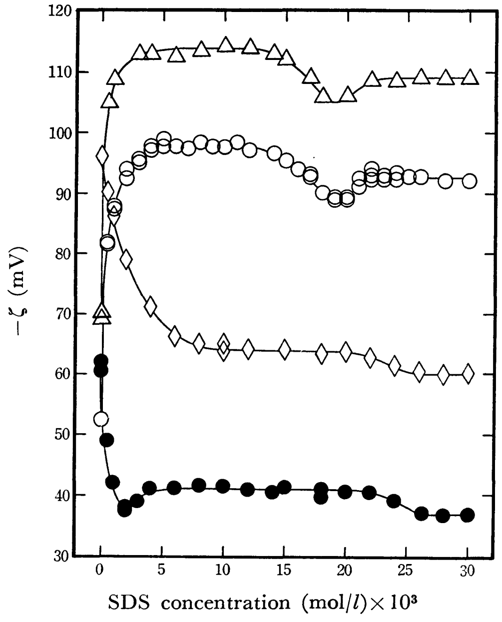

Fig. 4. ζ-Potentials of synthetic fibers in SDS solution (25°C).

(△) Pylen; (○) Nylon 6; (◇) Cashimilon; (●) Vinylon.

The ζ values obtained were all negative and changed rapidly with an increase in the SDS concentration, but remained approximately constant near and above the CMC. As the solution became more concentrated, they gradually changed again and thereafter, passing a minimum or a

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*4 It is believed that the coefficient B 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 coefficient B would be a negative quantity.[17,22]

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

break, became nearly constant again. The concentration of the minimum or the break at high concentrations roughly corresponded to that of the break of the η_{spm}/c_m vs. c_m curve (*cf.* Fig. 1 in Ref. 6). It was, consequently, suggested that the change in ζ-potentials at high concentrations may be connected with that in the structure of the SDS micelle.[7]

ζ-Potentials of Synthetic Fibers in an Aqueous STS Solution. *i) ζ-Potentials below the CMC.* The results obtained are shown in Fig. 5.

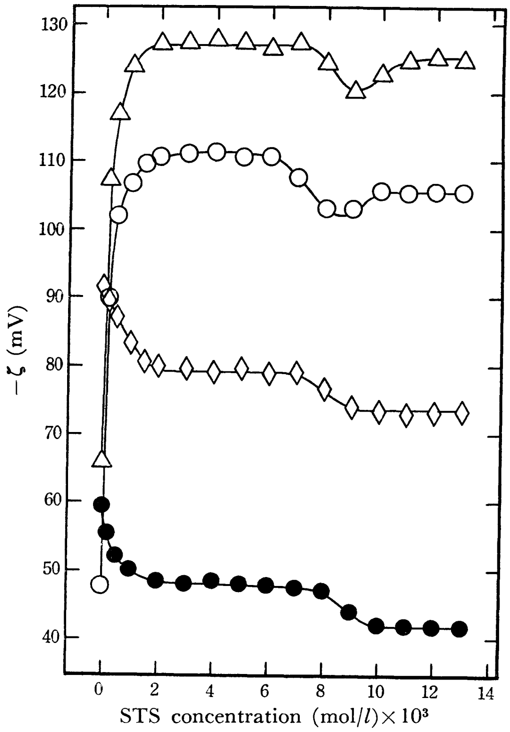

Fig. 5. ζ-Potentials of synthetic fibers in STS solution (40°C).
(△) Pylen; (○) Nylon 6; (◇) Cashimilon; (●) Vinylon.

The ζ-potentials (negative) for Pylen and Nylon 6 fibers increased sharply with an increase in the STS concentration below the CMC. This fact suggests that the amounts of STS adsorbed on the surfaces of these fibers rapidly increase with an increase in the agent concentration. The absolute ζ values of this system were considerably larger than those of the SDS system. It may, therefore, be suggested that the interaction between the hydrocarbon chain of the anionic surfactant and the hydrophobic part of fibers is important for the adsorption of the agent on the fibers.[3]

On the other hand, the ζ-potential (negative) for Cashimilon fiber decreased with an increase in the STS concentration. The decrease in ζ values with an increase in the concentration may be due to the compression of the diffuse double layer, because the total ionic strength in solutions increases with an increase in the concentration. The behavior of the ζ-potential for Vinylon fiber was similar to that obtained for Cashimilon fiber.

ii) ζ-Potentials above the CMC. The ζ values of the fibers examined remained nearly constant for some distance above the CMC. It can, therefore, be presumed that the surface adsorptions of STS on the fibers remain approximately constant in the range of concentrations larger than the CMC.

As the solution became more concentrated, the ζ values gradually changed again and thereafter, passing a minimum or a break, became constant once more. It is worth noting that the concentration of the minimum or the break observed corresponds roughly to those of the break of the η_{spm}/c_m vs. c_m curve (*cf.* Fig. 4 in Ref. 6) and of point β (*cf.* Fig. 6 in Ref. 6).

From these facts, it may be assumed that if the structure of the STS micelle in an aqueous solution changed at the concentration for the break or at that for point β, the structure of the diffuse double layer would be variable, resulting in a change of the ζ-potentials of the fibers.

In the more concentrated solutions, the properties of the STS micelle are invariable over a relatively wide range of concentration, suggesting that the size and the shape of the micelle remain nearly constant, as is shown by the viscosity data.[6] It can, therefore, be understood that the ζ-potentials of fibers are kept constant again at a high concentration, for the structure of the double layer is stable.

ζ-Potentials of Synthetic Fibers in an Aqueous SHS Solution. *i) ζ-Potentials below the CMC.* As is shown by Fig. 6, the variations in the ζ-potential (negative) with the concentration for Pylen and Nylon 6 fibers in an aqueous SHS solution were depicted by curves similar to those of SDS and STS systems. The absolute values of the ζ of the SHS system were appreciably larger than those of the latter. It may, therefore, be suggested that these fibers combine mainly with the SHS anion by means of the van der Waals force.[3]

On the other hand, the ζ-potential (negative) of Cashimilon or Vinylon fiber increased with an increase in the SHS concentration and thereafter, passing a maximum, gradually decreased with the concentration. This behavior was fairly different from that of the SDS and STS systems. The difference seems to result from the fact that the adsorption properties of the SHS anion on the fiber are superior to those of the SDS and STS anions.[3]

ii) ζ-Potentials above the CMC. The relation between the ζ-potentials and the surfactant concentrations of this system was very similar to those of the SDS and STS systems. The constancy of the ζ-potentials, therefore, implies that the sur-

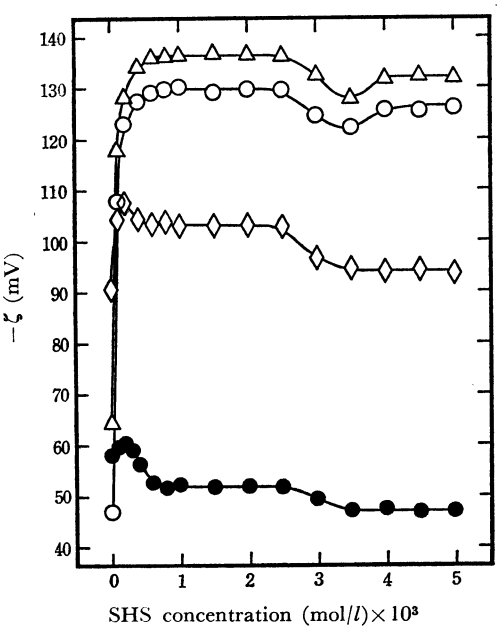

Fig. 6. ζ-Potentials of synthetic fibers in SHS solution (45°C).
(△) Pylen; (○) Nylon 6; (◇) Cashimilon; (●) Vinylon.

face SHS adsorptions on the fibers are unchanged in the range of concentration of (0.6—2.5)×10^{-3} mol/*l*. It may also be suggested that the surface-surfactant adsorptions of this system are considerably larger than those of the SDS and STS systems, because the absolute ζ values of this system are considerably larger than those of the latter above the CMC, as well as below it. The surfactant concentration corresponding to a minimum or a break in the ζ *vs.* concentration curves is very consistent with that of the break in the η_{spm}/c_m *vs.* c_m curve and that of point b in Fig. 3. It can, consequently, be presumed that the change in ζ-potentials above the CMC is connected with that in the structure of the SHS micelle.

In more concentrated solutions, the ζ values again became constant. This fact may be correlated with the stable structure of the diffuse double layer, as has been mentioned for SDS[7] and STS systems.

Mixed Micelle Compositions and CMC of Mixed Sodium Alkyl Sulfates

Mysels and Otter[23] suggested, from the conductivity data on aqueous solutions of pure sodium decyl and dodecyl sulfates and their mixtures, that the micelles initially formed are strongly enriched by the higher homolog, that the micellar compositions continue to change even after the CMC has been exceeded severalfold, and that, at higher concentrations, they tend to return to the initial composition. Tokiwa *et al.*[24] and Shedlovsky *et al.*[25] determined the mixed micelle compositions of the SDS-STS system. Their results were similar to those of Mysels and Otter.

In this study, the mixed micelle compositions of the SDS-STS and STS-SHS systems were determined in the same way as was used by Mysels and Otter; the results are shown in Figs. 7—10. It can be seen from Figs. 8 and 10 that the results are similar to those of Mysels and Otter. It can, consequently, be understood why some conclusions drawn from these results show a marked resemblance to those of Mysels and Otter.

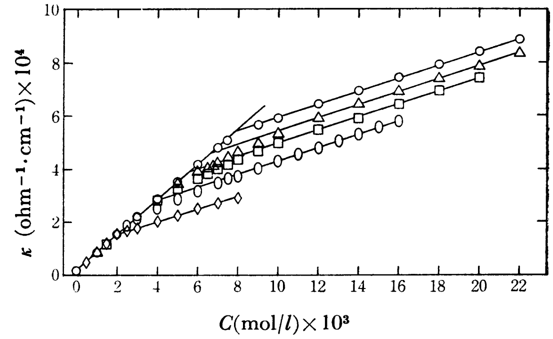

Fig. 7. Relation of specific conductivities (κ) to surfactant concentration (*c*) in SDS-STS mixed system (25°C).
mole% of lower homolog:
(○) 100; (△) 85; (□) 75; (0) 50; (◇) 0.

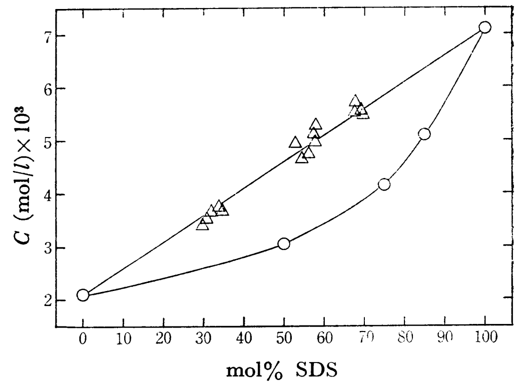

Fig. 8. Mixed micelle compositions (upper line) and CMC values (lower curve) in SDS-STS mixed system (25°C).

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[23] K. J. Mysels and R. J. Otter, *J. Colloid Sci.*, **16**, 462 (1961).

[24] F. Tokiwa, K. Ohki and I. Kokubo, This Bulletin, **41**, 2845 (1968).

[25] L. Shedlovsky, C. W. Jakob and M. B. Epstein, *J. Phys. Chem.*, **67**, 2075 (1963).

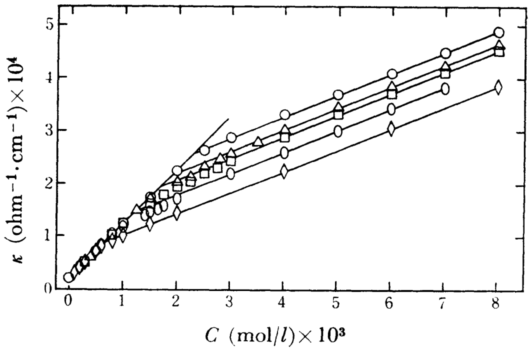

Fig. 9. Relation of specific conductivities (κ) to surfactant concentration (C) in STS-SHS mixed system (45°C).
mole % of lower homolog:
(○) 100; (△) 85; (□) 75; (0) 50; (◇) 0.

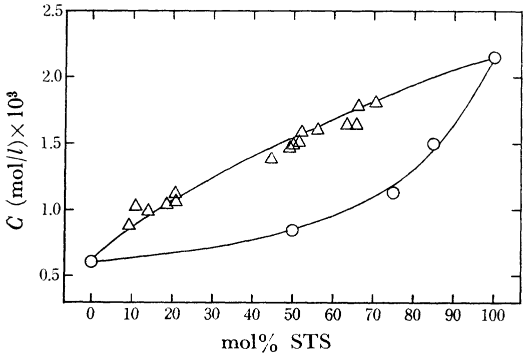

Fig. 10. Mixed micelle compositions (upper curve) and CMC values (lower curve) in STS-SHS mixed system (45°C).

ζ-Potentials of Fibers in Aqueous Solutions of Mixed Sodium Alkyl Sulfates

ζ-Potentials of Synthetic Fibers in an Aqueous Solution of the SDS-STS Mixture. *i) Mixed System Containing* 85 *mol% SDS.* The results obtained are shown in Fig. 11. The ζ-potential (negative) for Nylon 6 fiber rapidly increased with an increase in the concentration of the mixture below the CMC. This behavior was similar to that of the pure SDS and STS systems. However, the absolute ζ values of this mixed system were considerably larger than those of the pure SDS system, but smaller than those of the pure STS system. It can, therefore, be noted that the surface-adsorption properties of the higher homolog on the fiber are superior to those of the lower homolog.

On the other hand, the ζ-potential (negative) for Cashimilon fiber quickly decreased with an increase in the concentration and thereafter, passing a minimum, gradually increased. This behavior is different from that of the pure SDS and STS systems. It may be suggested that the decrease in the absolute ζ values is due to the compression of the double layer and that the increase is due to a preferential uptake of the higher homolog anions on the fiber. In the vicinity of the CMC, the ζ-potentials showed a maximum for each of the fibers. This may be due to the adsorption of the STS anion in preference to that of the SDS anion, because the concentration of the monomeric anion of the higher homolog reaches a maximum at the CMC.[23] Further, it may be due to the change in the mixed-micelle compositions.[23] However, it is not clear why the maximum appears in the vicinity of the CMC.

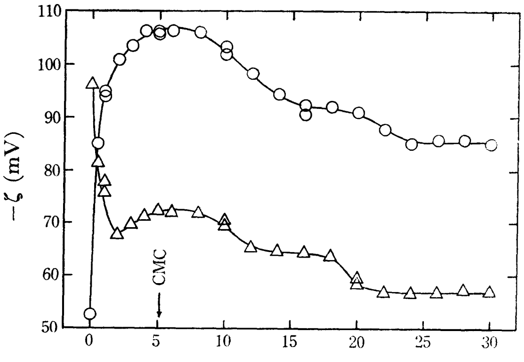

Fig. 11. ζ-Potentials of synthetic fibers in SDS-STS mixed system containing 85 mol% SDS (25°C).
(○) Nylon 6; (△) Cashimilon.

As the solution became more concentrated, the absolute ζ values of both the fibers decreased, step by step. This may be associated with the change in the compositions of the mixed micelles or with that in the compositions of the monomeric ions of the mixtures.

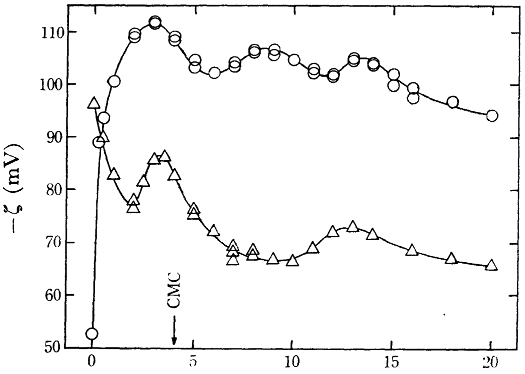

Fig. 12. ζ-Potentials of synthetic fibers in SDS-STS mixed system containing 75 mol % SDS (25°C).
(○) Nylon 6; (△) Cashimilon.

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26) D. W. Fuerstenau, *J. Phys. Chem.*, **60**, 981 (1956).

ii) Mixed System Containing 75 mol% SDS. The ζ-potentials of this system changed in a complicated fashion, showing a few maxima, with an increase in the concentration of the mixtures, as is shown by Fig. 12. The first maximum, in the vicinity of the CMC, seems to be due to the cause described in the previous section. The maximum observed at a slightly lower concentration than the CMC may at least partly be interpreted as follows: with an increase in the concentration, sufficient surfactant anions diffuse into the fiver-solution interface and are condensed there because of the increased adsorption; consequently, the adsorbed ions reach a certain critical concentration at the interface in the concentration range below the CMC.[26] A maximum corresponding to the second maximum of Nylon 6 fiber was not observed in the case of Cashimilon fiber. This may result from the difference between the adsorption properties of mixtures on the two fibers. The third maximum of Nylon 6 fiber corresponds to the second of Cashimilon fiber. It is, however, not clear why these maxima appear in the high concentration range.

iii) Mixed System Containing 50 mol% SDS. The ζ-potentials (negative) of both the fibers also showed a small maximum in the vicinity of the CMC, and thereafter decreased, step by step, with an increase in the concentration, as is shown in Fig. 13. The maximum was observed at a lower concentration than that of the former mixed system because of the decrease in the CMC. This is due to the cause mentioned in connection with the mixed system containing 85 mol% SDS. Further, it shifted somewhat to a lower concentration than the CMC. This partly results from the same cause, as has been described above. The step-by-step decrease in the ζ-potentials is connected with the change in the compositions of mixed micelles or with that in those of monomeric ions of the mixtures.

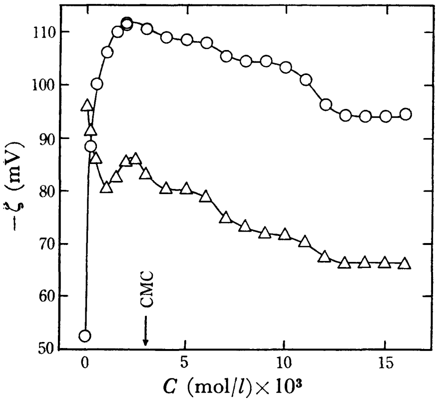

Fig. 13. ζ-Potentials of synthetic fibers in SDS-STS mixed system containing 50 mol% SDS (25°C).
(○) Nylon 6; (△) Cashimilon.

ζ-Potentials of Synthetic Fibers in Aqueous Solutions of STS-SHS Mixtures. The ζ-potentials of two synthetic fibers in mixed systems containing 85, 75 and 50 mol% STS are shown in Figs. 14, 15, and 16 respectively. The behavior of ζ-potentials for Nylon 6 fiber below the CMC was similar to those obtained in the pure STS and SHS systems, but the absolute values of ζ, which increased in the order of the composition: 85,

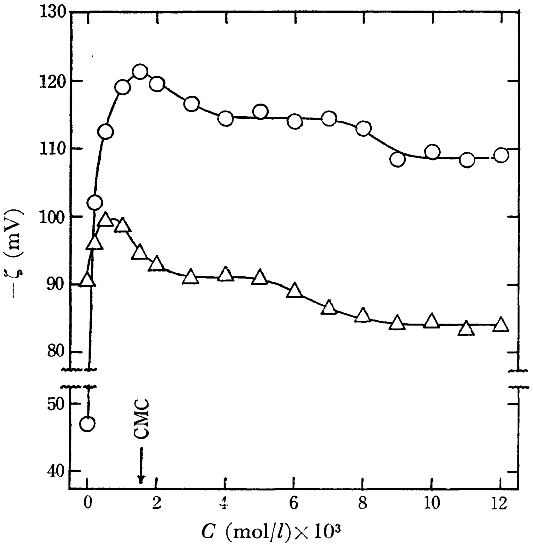

Fig. 14. ζ-Potentials of synthetic fibers in STS-SHS mixed system containing 85 mol % STS (45°C).
(○) Nylon 6; (△) Cashimilon.

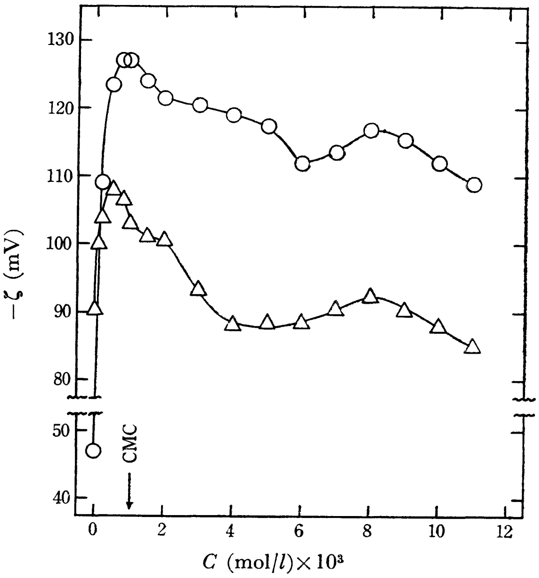

Fig. 15. ζ-Potentials of synthetic fibers in STS-SHS mixed system containing 75 mol % STS (45°C).
(○) Nylon 6; (△) Cashimilon.

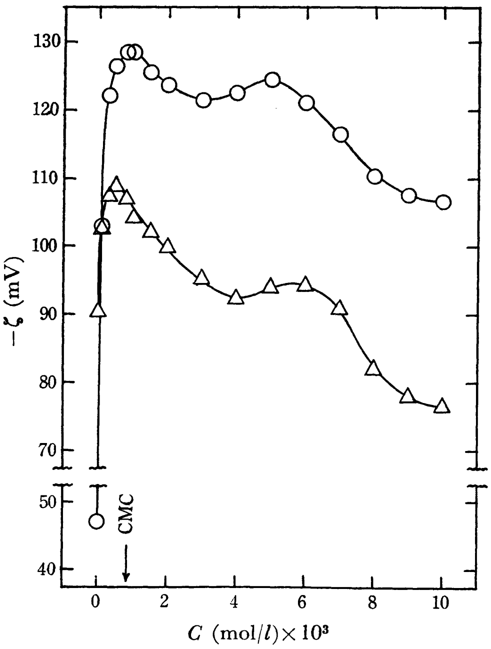

Fig. 16. ζ-Potentials of synthetic fibers in STS-SHS mixed system containing 50 mol % STS (45°C).
(○) Nylon 6; (△) Cashimilon.

75 and 50 mol% STS, were intermediate between those of the pure systems. The results suggest that the surface adsorptions of the higher homolog on the fiber are larger than those of the lower homolog.

On the other hand, the behavior of ζ-potentials for Cashimilon fiber below the CMC is similar to that of the pure SHS system, and different from that of the pure STS system. This results from the preferential adsorption of the SHS anion on the fiber.

In the vicinity of the CMC, a maximum of ζ-potentials for both the fibers was observed in all the mixed systems studied. The maximum shifted to low concentrations in the order of the composition: 85, 75 and 50 mol% STS, because of the decrease in the CMC. This may be attributed to the same cause as has been mentioned in connection with SDS-STS mixed systems.

As the solution became more concentrated, the absolute values of ζ for the mixed system containing 85 mol% STS decreased, step by step. This behavior was similar to that obtained for the mixed system containing 85 mol% SDS. It is connected with the change in the mixed micelle compositions or with that in the monomeric ion compositions of mixtures. On the other hand, the ζ-potentials of both the fibers in the mixed systems containing 75 and 50 mol% STS changed in an intricate manner, showing a maximum and a minimum, with an increase in the concentration of the mixtures. The behavior of the ζ-potentials is roughly analogous to that observed for the mixed system containing 75 mol% SDS.

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