The Solution State of Cationic Polysoap Derived from Polyallyl Chloride

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Polysoap differs from colloidal electrolytes in exhibiting no critical micelle concentration (CMC), and in it solubilization occurs over the entire polysoap concentration range. This means that a unit polymer specy in a true molecular solution acts as a micelle.[1]

In a preceding paper,[2] one of the present authors has already reported on the synthesis and some properties of cationic polysoaps, which consist of short polymer chains with chemically-attached soap-like groups. These polysoaps were prepared by quaternizing *N*-dodecylpiperidine or dimethyl dodecylamine with polyallyl chloride, and by quaternizing *N*-dodecylpiperidine with a copolymer of allyl chloride and vinyl acetate (1 : 1 molar ratio). Their CMCs in water were determined by the three independent methods, such as conductivity, dye absorption, and surface tension. The CMC values obtained by the three methods were in good agreement. From these results, it was concluded that the micelle formation of such a polysoap in water was indeed true.

The present work was undertaken in order to examine, by means of light-scattering and surface-tension measurements, the CMC, the micellar weight, the micellar charge in water and surface excess at the air-solution interface of a cationic polysoap which consists of a

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[1] M. E. L. McBain and E. Hutchinson, "Solubilization and Related Phenomena," Academic Press, New York (1955), p. 236.

[2] H. Narasaki, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **65**, 793 (1962).

relatively short polymer chain. Moreover, the results involved the effect of added sodium chloride on them.

Experimental

Material. — Polyallyl chloride was prepared by polymerizing allyl chloride at 65°C for 75 hr., using benzoyl peroxide (5% by weight of the monomer) as a polymerization initiator in an atmosphere of nitrogen, then the unreacted monomer was removed by steam distillation. The number-average molecular weight ($\overline{M}_n$) of the polyallyl chloride, as determined by freezing point depression in benzene, was 647, while the degree of polymerization ($\overline{P}_n$) calculated from $\overline{M}_n$ was 8.46. The chlorine content was 43.2% (calculated 46.4%) by a modification of the Volhard method.[3] The polysoap was prepared by quaternizing *N*-dodecylpiperidine with polyallyl chloride, using nitrobenzene as a solvent, at 150°C for 70 hr. in nitrogen. The reaction product was then isolated by precipitation into *n*-hexane. The precipitate was repeatedly washed with a large amount of benzene and dried at 55°C in a vacuum. Then it was obtained as a powder-like white material. This polysoap will be referred to as SP-100. The total chlorine content was 11.99%, as determined by a modification of the Volhard method, and the quaternized chlorine, as determined by the Volhard method, was 11.89%. Therefore, the degree of the quaternization of polyallyl chloride was calculated to be 99.2%, and the molecular weight of SP-100 was 2770.

Light Scattering.—Light-scattering measurements were carried out at a room temperature of about 25°C and with a wavelength of 436 mμ, by using a light-scattering photometer (Shimadzu Instr. Co.). The apparatus was calibrated against redistilled benzene as a reference standard. Scattered light was measured at 45°, 90° and 135° relative to the incident beam. The dissymmetry (Z_{45}) was determined for all solutions, only the solutions in which Z_{45} did not differ significantly from unity were used as light-scattering data. The Z_{45} of the pure solvent (water) clarified in the manner described below was less than 1.03. Therefore, it is thought that the optical clarification of the solvent is accomplished.

The optical clarification of the solution to be examined was achieved as follows. Stock solutions were prepared on a weight/volume basis. The solution was centrifuged for 1 hr. at 21000 g. and the upper 2/3 parts of the solution were used for the light-scattering measurements. Then aliquots of the solution thus obtained were diluted volumetrically. Redistilled water or an aqueous sodium chloride solution clarified by the above procedure was used as the solvent. After the prepared solutions had been allowed to stand overnight in order to assure equilibrium, they were then clarified by filtration, by using suction through an ultrafine sintered glass filter directly into a light-scattering cell.

The refractive index increments were determined with a differential refractometer (Shimadzu Instr. Co.) at a room temperature of about 25°C and with a wavelength of 436 mμ. The refractometer was standardized with an aqueous potassium chloride solution. The refractive index increments, dn/dc, of SP-100 were found to be effectively independent of the added sodium chloride concentration in the range from 0 to 0.3 mol./l., and the value was 0.175 ml./g.

For an accurate analysis, one should treat the light scattering data as a three-component system, for the present system which was composed of SP-100, water and sodium chloride. However, Strauss and Williams,[4] and Orofino and Flory[5] have suggested that hardly any relative errors in the molecular weight of polysoaps and polyelectrolytes between two component and three component treatments, can be found. Therefore, we treated it as a two-component system composed of SP-100 and water.

In order to evaluate the micellar weight and the slope of the Debye plot of SP-100 from the light scattering data, the Debye equation below was used;

$$K(C-C_0)/(R_{90}-R_{90,\mathrm{CMC}})=1/M+2A_2(C-C_0)$$

$K=2\pi^2 n_0^2(\mathrm{d}n/\mathrm{d}c)^2/\boldsymbol{N}\lambda_0^4$, where R_{90} is the reduced intensity of the solution at 90°; $R_{90,\mathrm{CMC}}$ is R_{90} at the CMC; n_0 is the refractive index of the solvent; n is the refractive index of the solution; C is the surfactant concentration in g./ml.; λ_0 is the wavelength of the incident light in a vacuum; $\boldsymbol{N}$ is the Avogadro number; M is the micellar weight; A_2 is the apparent second virial coefficient and C_0 is the CMC.

Surface Tension.— Surface tension measurements were carried out by the drop-weight method in a thermostat maintained at 30.0+0.2°C by using the correction of Harkins and Brown.[6] In the measurement, about one minute was allowed for the formation of each drop of the solution, since it was clear from a preliminary experiment that the solutions reached a constant value one minute after the drop formation.

Results and Discussion

The reduced intensity of the aqueous solutions of SP-100 is plotted against the surfactant concentration in Fig. 1. The CMC was obtained from the inflection point on a curve. The scattering curve for SP-100 in water apparently shows two break points, as 0.10% and 0.22%. The CMC value in water, as determined by the minimum concentration of the surface tension, is in better agreement with 0.22% than with 0.10%, in terms of light scattering. However, this value (0.22%) gives discrepancies when compared with the system composed of added salt in the Debye plot. The Debye plot in water crosses many other

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[3] W. Kimura, ibid., **37**, 1310 (1934).

[4] U. P. Strauss and B. L. Williams, *J. Phys. Chem.*, **65**, 1390 (1961).

[5] T. A. Orofino and P. J. Flory, ibid., **63**, 283 (1959).

[6] W. D. Harkins and F. E. Brown, *J. Am. Chem. Soc.*, **41**, 499 (1919).

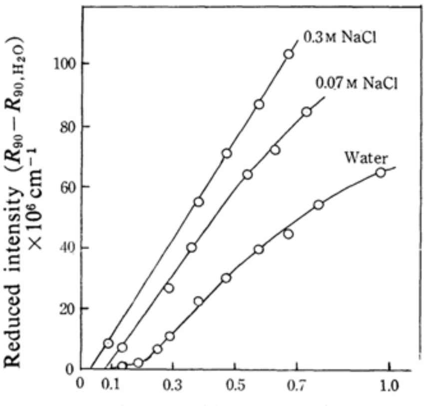

Fig. 1. Reduced intensity vs. concentration curves of SP-100 (wavelength 436 mμ, 25°C).

plots, and the extrapolation of the plot to the ordinate gives the micellar weight of about thirty thousand (Fig. 3). This means that, in the micellar weight vs. the molarity of sodium chloride relation (Fig. 4), a minimum exists at 0.03 M sodium chloride. On the other hand, the CMC value of 0.10% can easily explain the relation between the systems composed of water and of added salt in Fig. 3 and Fig. 4. Therefore, the CMC has been given as 0.10%.

The CMC of SP-100 (3.64×10^{-4} mol./l. in water) was much lower than the 10^{-2} mol./l. value of ordinary ionic monosoaps with the nearly same lipophilic properties, and it was of the same order of magnitude as those of nonionic monosoaps. It seems probable that a surfactant which has some soap-like groups in a molecule, such as SP-100, can more easily form a micelle than those which have only one soap group in a molecule.

As is shown in Fig. 2, when the logarithmic relation between the CMC and the total gegen ion concentration is plotted, the curve can be divided into two regions. One shows that added salt has little effect on the CMC at concentrations below about 0.07 mol./l. The other shows that the effect of added salt predominates beyond this concentration and that the CMC is linearly lowered with an increase in the total gegen ion concentration (cl^-). It is well known that the logarithmic relation between the CMC of a univalent ionic monosoap and the univalent gegen ion concentration can be expressed by the equation;

$$\log \mathrm{CMC} = A - B \log(\text{total gegen ion concn.})$$

where A and B are constants. The above phenomenon of SP-100 has never been observed for any ionic monosoaps. The dependence of the CMC of SP-100 on the total gegen ion concentration in the linear portion of the curve is given by;

$$\log \mathrm{CMC} = -4.122 - 0.547 \log (cl^-)$$
$$(0.07 \leqq (cl^-) \leqq 0.6\ \text{mol./l.})$$

$K(C-C_0)/(R_{90}-R_{90,\mathrm{CMC}})$ vs. $(C-C_0)$ curves are illustrated in Fig. 3. The plots form straight lines within this range of experimental accuracy. The uncertainties in the Debye plots can be seen in water, especially at lower micellar concentration of SP-100. The slopes of the Debye plots were smaller than those of ionic monosoaps.

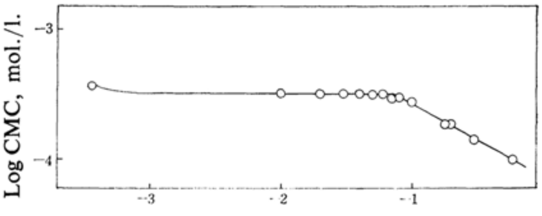

Fig. 2. Log CMC vs. log total gegen ion concentration curve of SP-100.

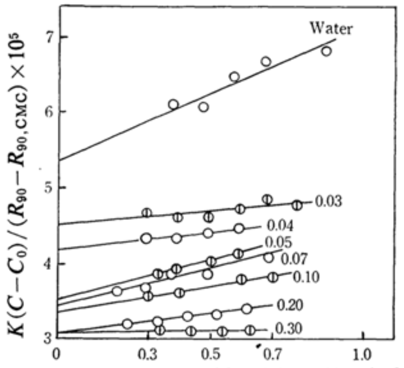

Fig. 3. Light-scattering of SP-100 in water and in aqueous sodium chloride solution (wavelength 436 mμ, 25°C). Numericals in this figure show the concn. of sodium chloride (mol./l.).

Strauss et al.[4] studied the transition from a typical polyelectrolyte to a polysoap of poly-4-vinylpyridine derivatives; they showed that a much more extended polyelectrolyte may be seen to have a much larger second virial coefficient. Inoue[7] pointed out that, in poly-2-vinylpyridine derivatives, the Huggins constant increased and the second virial coefficient decreased with an increase in their alkyl content. This reflects the interaction between their polar groups.

The micellar charge of SP-100 may, therefore, be expected to be quite small, though it may be improvable from the slope of the Debye plot. The charge on the micelle, p, can be

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[7] H. Inoue, *Kolloid-Z. U. Z. Polymere*, **195**, 102 (1964).

TABLE I. THE MICELLAR PROPERTIES OF SP-100 IN AQUEOUS SOLUTIONS

NaCl mol./l.	CMC mol./l. $\times 10^4$	M $\times 10^{-3}$	$1/AM_1$	B $\times 10^4$	$m(2)$	n $8.46\,m$	p	p/n
0	3.64	18.8	6.79	17.70	6.98	59.0	0.76	0.01
0.01	3.16	—	—	—	—	—	—	—
0.02	3.15	—	—	—	—	—	—	—
0.03	3.16	22.2	8.00	3.75	8.11	68.6	3.38	0.05
0.04	3.18	24.0	8.65	4.63	8.78	74.3	4.68	0.06
0.05	3.18	28.4	10.23	10.28	10.52	89.0	9.30	0.10
0.06	3.17	—	—	—	—	—	—	—
0.07	2.88	29.1	10.49	9.85	10.78	91.2	11.99	0.13
0.08	2.88	—	—	—	—	—	—	—
0.10	2.74	29.9	10.77	6.92	11.03	93.3	11.27	0.12
0.18	1.86	—	—	—	—	—	—	—
0.20	1.84	32.5	11.71	5.06	12.04	101.8	14.87	0.15
0.30	1.43	32.3	11.64	0.42	11.76	99.5	5.16	0.05
0.60	0.99	—	—	—	—	—	—	—

M: Micellar weight
$1/AM_1$: Apparent aggregation number; A=intercept of the Debye plot, and M_1=formula weight of SP-100
B: Slope of the Debye plot
$m(2)$: Aggregation number as computed from Eq. 2
n: Number of soap-like groups per micelle of SP-100
p: Micellar charge

obtained from the derived equation of Princen and Mysels[8] as follows;

$$p=[BM_1(n_1+fn_3)+\sqrt{2B(n_1+n_3)}]/A(1-AM_1E/2) \quad (1)$$

$$E=(n_1+fn_3)/(n_1+n_3)$$

where B is the slope of the Debye plot; M_1 is the formula weight of the surfactant; n_1 and n_3 are the CMC and the added simple salt concentration both in mol./ml. respectively; A is the intercept of the Debye plot, and f is the ratio of the molar refractive index increment of the added salt to that of the surfactant. Once the charge has been computed, the aggregation number, m, is given by;

$$m=\frac{1}{2}(pE+1/AM_1)+\frac{1}{2}\sqrt{(pE+1/AM_1)^2-(p^2+p)E^2} \quad (2)$$

The results thus obtained are represented in Table I. At a lower concentration range of added salt, the p/n value is much smaller than those values found for ionic monosoaps. This result may certainly be interpreted as follows. The SP-100 molecules interpenetrate each other in the interior of the micelle, and so the mutual repulsive force between the polar groups in the micelle is weakened by the shielding effect of the lipophilic groups. Many of the charged polar heads are buried so deeply in the interior of the micelle that they are effectively shielded. As a result of this shielding effect, the net charge on the micelle may be small even if the charge on single molecules is larger. On the other hand, the micellar charge increases with an increase in the added salt concentration, as is indicated in Table I. It seems probable that the micellar charge increases with the number of polar groups on the micellar surface, because the aggregated configuration of molecules in a micelle can be altered from the "*interpenetrated*" form mentioned above to a more regular one.

As Fig. 4 shows, it is noteworthy that the micellar weight of SP-100 increases much

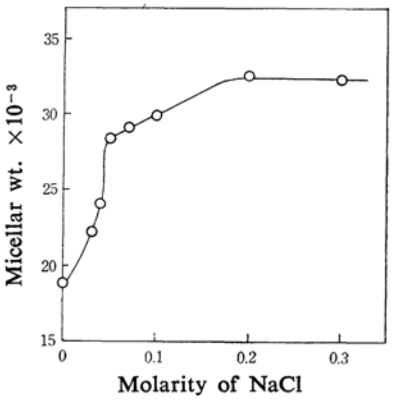

Fig. 4. Dependence of the micellar weight of SP-100 on the concentration of sodium chloride.

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[8] L. I. Osipow, "Surface Chemistry," Reinhold Publishing Co., New York (1962), p. 176; L. H. Princen and K. J. Mysels, *J. Colloid Sci.*, 12, 594 (1957).

faster with an increase in the concentration of salt below about 0.06 M. On the contrary, the CMC remained essentially constant in the range from 0.01 to 0.07 M of salt. It is well known that, in ionic monosoap solutions, the addition of salt decreases the CMC and increases the micellar weight. The discrepancy between the CMC and micellar growth of SP-100 in the diluted salt solutions may be interpreted as follows. The effect of the addition of salt on the CMC and on the micellar weight of SP-100 may be distinguished as two concentration ranges. One holds in the case of the diluted SP-100 solutions below the CMC, while the other holds with solutions more concentrated than the CMC. Nakagawa and Inoue[9] considered theoretically that an intramolecular association between alkyl groups would occur in a polysoap, which did not aggregate between the molecules, even in a quite diluted solution when the cohesive power between alkyl groups was extremely strong. The degree of association between alkyl groups is large under some conditions, even in the case of a polysoap with fewer soap-like groups. In view of this, it is probable that an intramolecular association between dodecyl groups of a SP-100 molecule occurs. A small amount of added salt can not give a cohesive power level, whom SP-100 molecules require to form a micelle, to the SP-100 molecules at the lower concentrations of SP-100 just below the CMC, because the intramolecular association is expected to predominate at the lower concentrations of SP-100. Cohesive power sufficient to form a micelle may not be given to the molecules in the solution before the salt concentrtion reaches 0.07 M. On the other hand, upon the addition of a small amount of salt, the micellar weight of SP-100 increases much faster with an increase in the concentration of salt in the case of higher surfactant concentrations, because of the accessibility between the SP-100 molecules in the solution.

Surface tension vs. the logarithm of the SP-100 concentration curves are given in Fig. 5. The uppermost curve shows the system composed of water, while the lowest two curves illustrate the effect of the presence of sodium chloride on the surface activity of the surfactant. Surface tension can be regarded as entirely a linear function of $\log C$ in the concentration range of the surfactant below but near the CMC, and the $-d\gamma/d\log C$ values in these three curves are in fair agreement.

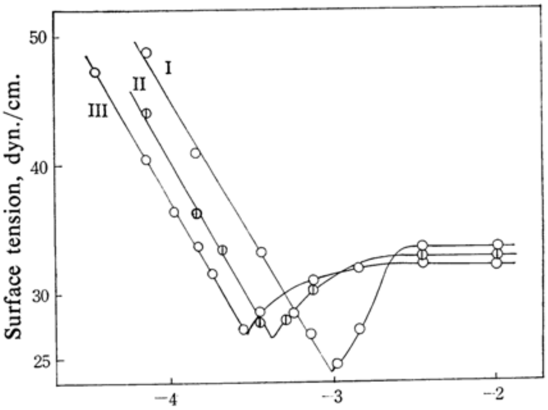

Fig. 5. Surface tension vs. log concentration curves of SP-100 at 30°C.
I Distilled water II 0.05 M NaCl
III 0.10 M NaCl

The slope of the surface tension vs. the logarithm of the concentration of an ionic surfactant has different physical meanings under various conditions. The surface excess of SP-100 at the air-solution interface can be determined from the slope of the surface tension vs. the logarithm of the SP-100 concentration containing a definite amount of sodium chloride. In this case, Gibbs adsorption isotherm is expressed by Shinoda and Nakayama[10] as

$$-d\gamma/\boldsymbol{RT}\,d\ln X_2=\Gamma_2+(X_2/X_3)\Gamma_3 \qquad (3)$$

where γ is the surface tension; $\boldsymbol{R}$ is the gas constant; T is the absolute temperature; Γ_2 and Γ_3 are the surface excesses of the surfactant ion and the gegen ion at the air-solution interface respectively; and X_2 and X_3 are the mole fractions of components. Because X_3 is much larger than X_2 in the concentration region of SP-100 examined, and since Γ_3 is supposed to be at most commensurate with Γ_2, Eq. 3 reduces to

$$-d\gamma/\boldsymbol{RT}\,d\ln X_2=\Gamma_2 \qquad (4)$$

Strictly speaking, the sample must be purified until it shows no minimum in γ - $\log C$ curves. However, in the present system, it is difficult for us to do so; moreover, the sample itself includes fatal uncertainties in molecular weight distribution, quaternized degree distribution, and end group, etc. Therefore, we have greater interest in the comparison of the surface excesses of monosoaps and ordinary polysoaps than in the determination of the absolute value.

The Γ_2 value of SP-100, as calculated from Eq. 4 is 3.78×10^{-10} mol./cm²; the corresponding surface area (A) is obtained as 44 Å²/mol. by the equation of $A=10^{16}/\boldsymbol{N}\Gamma_2$, where $\boldsymbol{N}$ is the Avogadro number. The Γ_2 value is of the same order of magnitude as those found for

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[9] T. Nakagawa and H. Inoue, *Kolloid-Z. u. Z. Polymere*, **195**, 93 (1964).

[10] K. Shinoda and H. Nakayama, *J. Colloid Sci.*, **18**, 705 (1963).

ordinary ionic monosoaps. However, since the molecular weight of SP-100 is of the order of 10^3, as determined on a weight basis, the surface excess of SP-100 is much larger than those of ionic monosoaps.

Summary

Cationic polysoap (SP-100, mol. wt. 2770), consisting of a short polymer chain with chemically-attached soap-like groups, has been prepared by quaternizing *N*-dodecylpiperidine with polyallyl chloride (mol. wt. 647). Some properties of the aqueous solution of SP-100 has been investigated by the light-scattering and surface-tension methods in the absence of and in the presence of sodium chloride.

We have found that the solution of such a polysoap exhibited the CMC value and that the concentration was 3.64×10^{-4} mol./l. (light scattering).

When the logarithmic relation between the CMC and the total gegen ion concentration was plotted, the curve thus obtained could be divided into two regions. Namely, the curve was almost flat at lower total gegen ion concentrations, followed by a depressed portion.

The micellar weight of SP-100 was 18800 in water and 32300 in a 0.3 M sodium chloride solution. The charges of SP-100 in aqueous solutions were calculated from the slope of the Debye plots by the derived equation of Princen and Mysels; on the basis of these results, the micellar charge of SP-100 in water is quite small.

The surface excess (Γ_2), together with the corresponding surface area (A), of SP-100 at the air-solution interface has been calculated from the slopes of the surface tension vs. the logarithm of polysoap concentration curve slightly below the CMC by applying the Gibbs equation. The Γ_2 value thus obtained was 3.78×10^{-10} mol./cm^2, while A was 44 Å^2/mol. The Γ_2 value of SP-100 in mol./cm^2 was of nearly the same order of magnitude as those of ionic monosoaps.

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