

Micelle Formation of Oil-Soluble Surfactants in Nonaqueous Solutions: Effect of Molecular Structure of Surfactants

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Received October 12, 1970; accepted November 12, 1970

The micellar weight of dialkylsulfosuccinates, dialkyldimethylammonium halides, and polyoxyethylene 2(1,3-dioctoxypropyl) ether in nonaqueous solutions was measured by the vapor pressure depression method. The apparent aggregation number of anionic surfactants approached saturation values above a fixed range of concentration, whereas that of cationic surfactants generally increased with increase of concentration. However, the nonionic surfactant formed no micelles in various solvents. The aggregation number (λ) of both anionic and cationic surfactants generally decreased with increase in the total carbon number of the alkyl group. The aggregation number of the anionic surfactant having the less bulky hydrocarbon group was larger than that of the anionic surfactant having the more bulky hydrocarbon group. The order of magnitude of λ of surfactants having hydrocarbon groups of equal size was anionics \gg cationics $>$ nonionics in various solvents. These results were compared with the results reported by other authors.

INTRODUCTION

It is well known that an oil-soluble surfactant forms micelles in a nonaqueous solution as well as in an aqueous solution. The micellar behavior of the surfactant in nonpolar solvents differs markedly from that in aqueous surfactant solutions. For instance, the micellar size in benzene solutions ranges from the monomer of nonionic surfactants (1, 2), to the high linear polymer of dry phenylstearate (3). It is well recognized that the driving force and the size-limiting factor for micelle formation in nonaqueous systems are mainly the attraction between polar groups and the steric hindrance of the hydrocarbon groups of surfactants, respectively. However, the effect of the polar groups and that of the size of hydrocarbon groups of surfactants on micelle formation in nonaqueous solutions have not been studied systematically.

In this study, in order to investigate the effect of the molecular structure of surfactants on micelle formation in nonaqueous systems, the micellar weight of sulfonated

anionic surfactants, quaternized cationic surfactants, and a polyoxyethylated nonionic surfactant having hydrocarbon groups of equal size and that of anionic surfactants having hydrocarbon groups of various structures were measured by the vapor pressure depression method. The experimental results were compared with those of dialkyl-naphthalene sulfonates reported by Kaufman and Singleterry (4) and by Heilweil (5), triphenylmethyl benzene sulfonates reported by Reerink (6), and di-(2-ethylhexyl) sodium sulfosuccinate reported by Kitahara *et al.* (7), by Frank and Zografis (8), and by Peri (9).

EXPERIMENTAL

Materials. Di-(*n*-butyl) sodium sulfosuccinate (NaDnC_4S), di-(*n*-hexyl) sodium sulfosuccinate (NaDnC_6S), di-(*n*-octyl) sodium sulfosuccinate (NaDnC_8S), di-(1-methylheptyl) sodium sulfosuccinate (NaDIMC_7S), di-(2-ethylhexyl) sodium sulfosuccinate ($\text{NaD2EC}_6\text{S}$), di-(2,2,4-trimethylpentyl) sodium sulfosuccinate ($\text{NaD224TMC}_5\text{S}$),

di-(*n*-decyl) sodium sulfosuccinate (NaDn-C₁₀S), di-(*n*-dodecyl) sodium sulfosuccinate (NaDnC₁₂S), and di-(2-ethylhexyl) potassium sulfosuccinate (KD2EC₆S) were used as anionic surfactants. Details of preparation and the results of the elementary analysis of NaDnC₈S, NaD1MC₇S, NaD2EC₆S, and KD2EC₆S were described in the previous publication (10). Other anionic surfactants were synthesized as follows: Anhydride maleic acid was esterified with *n*-butyl alcohol (bp 117°–118°C), *n*-hexyl alcohol (bp 157.5°–160°C), *n*-decyl alcohol (bp 121°–122°C/18 mm Hg), *n*-dodecyl alcohol (bp 164°–166°C/43.5 mm Hg), or 2,2,4-trimethylpentyl alcohol in benzene or toluene with sulfuric acid as catalyzer. Each raw maleic ester was washed with 5% aqueous sodium carbonate solution and dried with anhydrous sodium carbonate in benzene or toluene. After benzene or toluene had been evaporated, the ester was distilled under the following conditions: di-*n*-butylmaleic ester: 123°–125°C/4.5 mm Hg; di-*n*-hexylmaleic ester: 159°–165°C/4.5 mm Hg; di-2,2,4-trimethylpentylmaleic ester: 168°–171°C/3.0 mm Hg; di-*n*-decylmaleic ester: 224°–225°C/3.0 mm Hg; and di-*n*-dodecylmaleic ester: 226°–227°C/1.5 mm Hg. Each maleic ester purified was sulfonated with 60% aqueous acid sodium sulfite solution. Each resultant surfactant was purified according to the method of Williams *et al.* (11). All the surfactants were white crystalline. The surface tension of NaDnC₈S, NaDnC₆S, and NaD224TMC₅S in distilled water at 25°C indicated no minimum and the c.m.c. values of 2.0×10^{-1} M for NaDnC₈S, 1.32×10^{-2} M for NaDnC₆S, and 3.45×10^{-3} M for NaD224TMC₅S were in good agreement with previously reported values (11). The results of the elementary analysis of the surfactants are shown in Table I.

Dialkyldimethylammonium chloride was prepared by quaternization of dimethyldodecylamine (98°–100°C/2.5 mm Hg), dimethyltetradecylamine (146°–148°C/2 mm Hg), dimethylhexadecylamine (140°–142°C/1.0 mm Hg), or dimethyloctadecylamine (162.5°–163°C/1.5 mm Hg) with *n*-alkylchloride of Extra Pure reagent grade in ampoules. The surfactant obtained was

TABLE I
THE RESULTS OF THE ELEMENTARY ANALYSIS OF ANIONIC SURFACTANTS

Surfactant	Na (%)		S (%)	
	Expt	Calcd	Expt	Calcd
Di-(<i>n</i> -butyl) sodium sulfosuccinate	6.92	6.92	9.20	9.65
Di-(<i>n</i> -hexyl) sodium sulfosuccinate	5.99	5.92	7.61	8.25
Di(2,2,4-trimethylpentyl) sodium sulfosuccinate	5.47	5.17	5.60	7.21
Di-(<i>n</i> -decyl) sodium sulfosuccinate	4.43	4.56	5.67	5.82
Di-(<i>n</i> -dodecyl) sodium sulfosuccinate	3.96	4.13	5.00	5.76

purified by recrystallization from ethyl acetate. The results of the elementary analysis of surfactants are shown in Table II. Details of the preparation and the purification and the results of the elementary analysis of dialkyldimethylammonium bromides, dialkyldimethylammonium iodides, di-2-ethylhexylammonium bromide (D2EC₆-ABr), and polyoxyethylene 2(1,3-dioctoxypropyl) ether ($n = 9.2$) (DC₈P(EO)_{9.2}H) were described in the previous publications (10, 12, 13). Cyclohexane, benzene, *n*-heptane, isooctane, and carbon tetrachloride of Guaranteed reagent grade were purified according to the procedure described previously (14, 15).

Measurements. The apparent molecular weight of surfactants was measured by the vapor pressure depression method with a Hidachi-Perkin-Elmer Molecular Weight Measuring Apparatus Type 115. The calibration curve relating the variation of $\log(\Delta R/C)$ to $\log(\text{molecular weight})$ was made with ethylstearate (mol wt = 312.5), trilaurine (mol wt = 639.0), and standard polystyrenes of known molecular weight (316, 639, 900, 2,030, 4,800, 10,500, and 20,400), where ΔR is the resistance difference between the pure solvent and the solution and C is the concentration of the solution. Surfactant solutions ranging from about 2 to 100 (millimoles/kilogram solvent) were prepared after all the surfactants had

TABLE II
THE RESULTS OF THE ELEMENTARY ANALYSIS OF CATIONIC SURFACTANTS

	C(%)		H(%)		N(%)	
	Expt	Calcd	Expt	Calcd	Expt	Calcd
Propyldodecyldimethylammonium chloride	66.64	69.94	13.82	13.12	4.32	4.35
Butyldodecyldimethylammonium chloride	69.09	70.66	13.25	13.18	4.54	4.58
Didodecyldimethylammonium chloride	73.93	74.68	13.81	13.50	3.56	3.34
Dodecyltetradecyldimethylammonium chloride	71.50	75.36	13.88	13.55	3.12	3.14
Dodecyloctadecyldimethylammonium chloride	70.64	76.51	13.51	13.64	2.97	2.79
Dihexadecyldimethylammonium chloride	72.95	76.99	13.88	13.68	1.58	2.64
Hexadecyloctadecyldimethylammonium chloride	75.16	77.43	14.05	13.72	2.72	2.51
Dioctadecyldimethylammonium chloride	74.47	77.82	13.14	13.75	2.71	2.39

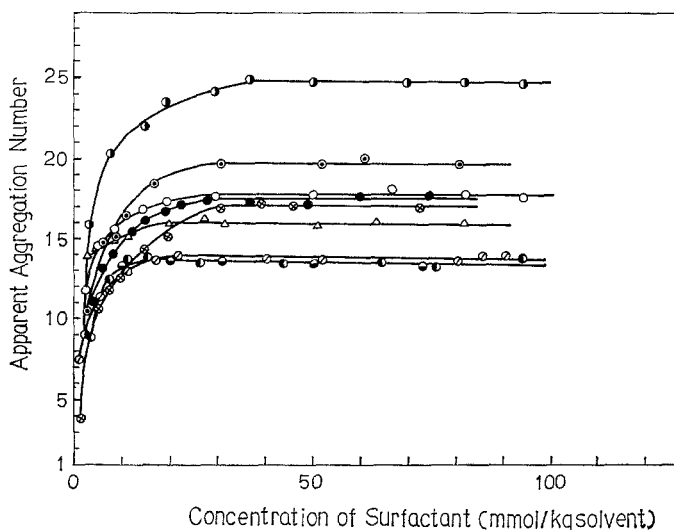


FIG. 1. Relationship between apparent aggregation number and concentration of anionic surfactants. \odot : NaDnC_4S ; \ominus : NaDnC_6S ; \circ : NaDnC_8S ; \bullet : $\text{NaDnC}_{10}\text{S}$; \otimes : $\text{NaDnC}_{12}\text{S}$; \oslash : $\text{NaD1MC}_7\text{S}$; \ominus : $\text{NaD2EC}_6\text{S}$; \bullet : $\text{NaD224TMC}_6\text{S}$; \triangle : $\text{KD2EC}_6\text{S}$.

been dried at 80°C in 3 mm Hg for 8 hrs. They were kept at room temperature overnight in a desiccator and the measurement was done in order of increasing concentration.

The molar ratio of water to the surfactant in the surfactant solution was below 0.1. In the case of nonaqueous systems, water often greatly affects micelle formation. Kitahara (16) and Sirianni *et al.* (17) demonstrated that a small content of water has no effect on the micellar weight in nonionic surfactant solutions. Corkill *et al.* (18) reported that number-average micellar weight is not affected by a small content of water in ionic surfactant solutions. Hence, no

attempt was made to remove further water. The temperature was kept at 40°C throughout the measurements.

RESULTS AND DISCUSSION

Dependence of Apparent Aggregation Number upon Surfactant Concentration. Representative examples of the dependence of apparent aggregation number upon the concentration of surfactants are shown in Figs. 1 and 2 for the benzene solutions of dialkylsulfosuccinates and dialkyldimethylammonium halides, respectively. As seen in Figs. 1 and 2, the apparent aggregation number of the anionic surfactants

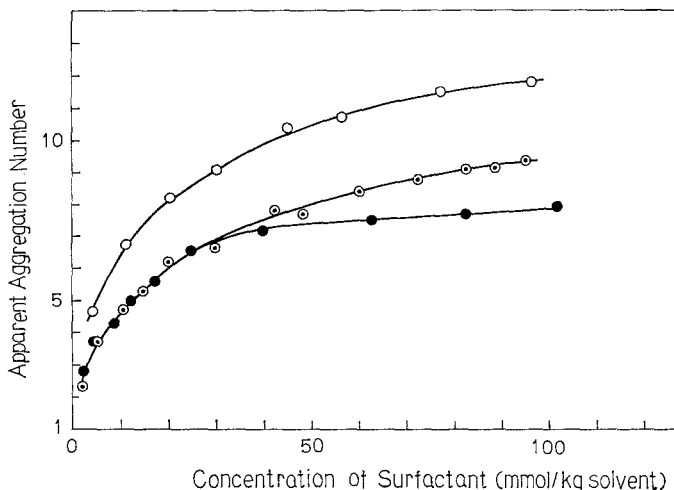


FIG. 2. Relationship between apparent aggregation number and concentration of cationic surfactants. \circ : $R_3R_{12}N(CH_3)_2Cl$; \odot : $R_3R_{12}N(CH_3)_7I$; \bullet : $R_{12}R_{16}N(CH_3)_2Br$.

approaches a saturation value above about 20–30 (millimoles/kilogram solvent), whereas that of cationic surfactants gradually increases with increase of the surfactant concentration. The concentration dependence of the apparent aggregation number for anionic surfactants in other solvents was also similar to the case of benzene solutions. The nonionic surfactant used here was molecularly dissolved in the present solvents, the apparent aggregation number being unity. Hence, the saturation apparent aggregation number was taken as the true aggregation number for anionic surfactants, whereas the true aggregation number for cationics was calculated by the following method (2).

Variation of Aggregation Number with Alkyl Group Size of Surfactants. In order to examine the variation of the aggregation number with the size of the alkyl group of dialkylsulfosuccinates and dialkyldimethylammonium halides in benzene solutions, the aggregation number of each of these surfactants was plotted against the total number of carbons in the alkyl group in Fig. 3. It is seen in Fig. 3 that the slope of the curve between the true aggregation number (λ) and the carbon number of the anionic surfactants is first abrupt (for $NaDnC_4S$ and $NaDnC_6S$) and afterwards gentle (for

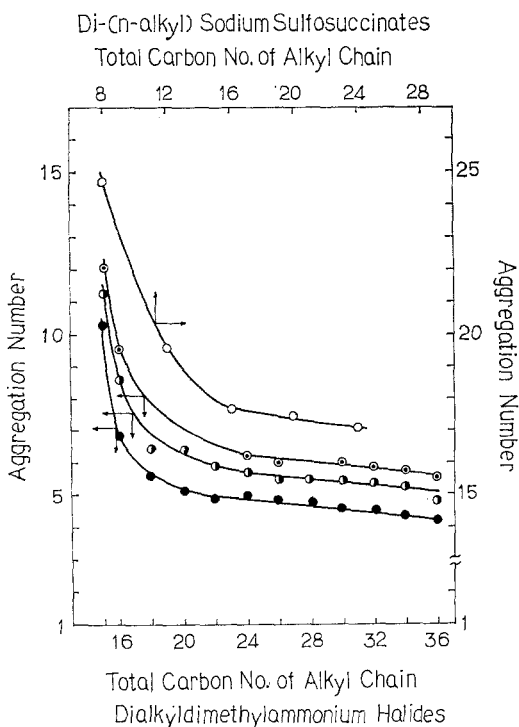


FIG. 3. Relationship between aggregation number and total carbon number of alkyl chain of surfactants. \circ : Dialkylsulfosuccinates; \odot : Dialkyldimethylammonium chlorides; \bullet : Dialkyldimethylammonium bromides; \bullet : Dialkyldimethylammonium iodides.

TABLE III

STERIC EFFECT OF HYDROCARBON GROUPS AND COUNTER IONS EFFECT ON THE AGGREGATION NUMBER OF ANIONIC SURFACTANTS

Surfactant	Alkyl group of surfactant	Benzene	Carbon tetrachloride	Cyclohexane
NaDnC ₈ S	<i>n</i> -Octyl	17.7	27.4	—
DaD1MC ₇ S	1-Methylheptyl	13.8	20.6	18.4
NaD2EC ₆ S	2-Ethylhexyl	13.6	19.6	18.2
NaD224TMC ₅ S	2,2,4-Trimethylpentyl	13.6	—	—
KD2EC ₆ S	2-Ethylhexyl	16.0	21.4	22.9

NaDnC₈S, NaDnC₁₀S, and NaDnC₁₂S). For the cationic surfactants, values of λ for propyldodecyldimethylammonium halides are as high as 12.1, 11.3, and 10.3 for chloride, bromide, and iodide, respectively, but the values of λ for the other surfactants decrease gradually with increase of the total carbon number. It may be suggested that the driving force between polar groups of surfactants for micellization surmounts the dispersion force between alkyl group and solvent hydrocarbon for the shorter surfactants, but that with increase of the alkyl chain of the hydrocarbon group the dispersion force oppositely surmounts the driving force.

Values of λ for NaDnC₈S, NaDnC₁₀S, and NaDnC₁₂S in Fig. 1, which are slightly different, are compared with those of sodium dinonylnaphthalene sulfonate (NaDNNS) and sodium didodecyl naphthalene sulfonate (NaDDNS) in benzene solutions reported by Kaufman *et al.* (4) and Heilweil (5). The latter ($\lambda = 12$ for NaDNNS and $\lambda = 9.7$ for NaDDNS) are lower than the former ($\lambda = 17.7$ for NaDnC₈S, $\lambda = 17.5$ for NaDnC₁₀S, and $\lambda = 17.1$ for NaDnC₁₂S). However, the tendency of decrease of λ with increase of alkyl chain length is similar for both groups. The above difference in λ may be due to the difference of solubility in benzene between the ester group associated with the dialkylsulfosuccinates and the naphthalene group associated with the dinonylnaphthalene sulfonates.

Steric Effect of Hydrocarbon Group and Counter Ion Effect of Anionic Surfactants. For both the anionic and cationic surfactants, as seen in Fig. 3, steric effects with the hydrocarbon group have been observed in a difference of λ between surfactants having

shorter and longer alkyl chains, but those associated with the symmetry or dissymmetry of the alkyl group of cationic surfactants were hardly apparent for surfactants having a longer alkyl chain. Hence, in order to examine the steric effect of alkyl groups having an equal carbon number in anionic surfactant molecules, values of λ for NaDnC₈S, NaD1MC₇S, NaD2EC₆S, and NaD224TMC₅S were compared in various solvents as seen in Table III. The λ of KD2EC₆S was also presented in the table in order to examine the effect of the counter ion. The value of λ for NaDnC₈S having a less bulky alkyl group is larger than that of NaD1MC₇S, NaD2EC₆S, or NaD224TMC₅S, each having a more bulky alkyl group, though the difference of λ among NaD1MC₇S, NaD2EC₆S, and NaD224TMC₅S is hardly evident. It is also evident from comparison of λ among NaDnC₆S, NaDnC₈S, and NaD2EC₆S that the bulky ethyl side chain associated with NaD2EC₆S limits the growth of nonaqueous micelles. The difference in magnitude of λ among NaDn₆S, NaDnC₈S, and NaD2EC₆S has been observed in *n*-octane solutions as reported by Frank and Zografi (8).

On the other hand, if the micelle formation in the nonaqueous system is promoted by the interionic force between the counter ion and the neighboring surfactant ion, λ of NaD2EC₆S (having a smaller cationic radius) should have a larger value than that of KD2EC₆S. The experimental result in Table III was opposite to the expectation. This fact may indicate that the steric effect of the D2EC₆S ion surmounts the effect of the size of the cation. That is, the D2EC₆S ion may interfere more strongly with the growth of micelles for NaD2EC₆S having the smaller cation. The abnormal behavior of λ due to

TABLE IV
COMPARISON OF AGGREGATION NUMBERS AMONG ANIONIC, CATIONIC, AND NONIONIC SURFACTANTS AND SOLVENT DEPENDENCE OF AGGREGATION NUMBER

Solvent	δ^a	NaD2EC ₆ S	D2EC ₆ ABr	DC ₈ P (EO) _{9.2} H
Benzene	9.15	13.6	2.3	1.0
Carbon tetra- chloride	8.6	20.6	2.2	1.0
Cyclohexane	8.2	18.2	4.0	1.0
<i>n</i> -Heptane	7.45	21	4.7	1.0
Isooctane	6.85	21	4.7	1.0

^a δ : Solubility parameter of solvents at 25°C.

the difference of the counter ion was found for potassium and sodium (tripentylmethyl) benzene sulfonates (K or NaTPMBS) reported by Reerink (6). Thus, the micellar size of KTPMBS was strongly dependent on the concentration, whereas that of NaTPMBS was independent of the concentration.

Comparison among Anionic, Cationic, and Nonionic Surfactants and Solvent Dependence of λ . Since the polar group of surfactants is recognized as the main driving force on the nonaqueous micellization, it is interesting to compare the micellar size among anionic, cationic, and nonionic surfactants having a similar hydrocarbon group. Values of λ of NaD2EC₆S, D2EC₆ABr, and DC₈P(EO)_{9.2}H

in various solvents are presented in Table IV. The order of magnitude of λ was anionic \gg cationic $>$ nonionic surfactants in every solvent. Furthermore, a comparison of λ among cationics can be made from Fig. 3, the decreasing order of λ being chlorides $>$ bromides $>$ iodides. These results of the order of λ are explicable by the strength of the interaction force between polar groups of surfactant molecules.

It is also observed from Table IV that λ of both the anionic and cationic surfactants decreases with increase of the solubility parameter of the solvents. This behavior is consistent with that for dinonylnaphthalene sulfonates reported by Little and Singleterry (19). Although nonionics may form micelles (21), Sirianni *et al.* (1), the present authors (2), and Becher (20) have reported that some nonionics do not form micelles. It is noticeable that the presence of a trace of water may be markedly effective for micelle formation of nonionics.

Comparison with Other Studies on Di-(2-ethylhexyl) Sodium Sulfosuccinate System. The solvent dependence of the micellar size of di-(2-ethylhexyl) sodium sulfosuccinate has been studied by Kitahara *et al.* (7), Frank and Zografi (8), and Peri (9) by use of light-scattering measurements. The dispersity of the micelle of NaD2EC₆S can be judged from the ratio of the weight-average micellar weight (\bar{M}_w) to the number-average micellar

TABLE V
COMPARISON WITH OTHER STUDIES ON THE DI-(2-ETHYLHEXYL) SODIUM SULFOSUCCINATE SYSTEM

Solvent	Aggregation no.	Temperature (°C)	Method ^a	\bar{M}_w/\bar{M}_n	Reference
Benzene	23	28 ± 4	L.S.	1.7	7
	13.6	40	V.P.		This work
Carbon tetrachloride	17	25	L.S.	0.8	9
	20.6	40	V.P.		This work
Cyclohexane	39	25	L.S.	2.1	8
	56	28 ± 4	L.S.	3.0	7
	18.2	40	V.P.		This work
Isooctane	20	25	L.S.	1.0	9
	21	40	V.P.		This work

^a L.S. Light-scattering method. V. P. Vapor pressure depression method.

weight (\bar{M}_n), obtained by the vapor pressure depression method. Results are summarized in Table V. The difference of the measurement temperature and the existence of errors in the light-scattering measurement of small micelles in nonaqueous systems, *i.e.*, the low turbidity and the low increment of refractive index with concentration, do not allow for quantitative comparison. However, the unity or approximate unity of \bar{M}_w/\bar{M}_n in isoctane or carbon tetrachloride is notable and suggests monodispersity of the nonaqueous micelle.

ACKNOWLEDGMENTS

The authors wish to thank Mr. M. Ozaki for the measurement of micellar weight and the Ministry of Education of Japan for partial financial support of this work.

REFERENCES

1. SIRIANNI, A. F., AND COLEMAN, R. D., *Can. J. Chem.* **42**, 682 (1964).
2. KON-NO, K. AND KITAHARA, A., *Kogyo Kagaku Zasshi* **68**, 2058 (1965).
3. HONIG, J. G., AND SINGLETERRY, C. R., *J. Phys. Chem.* **60**, 1108 (1956).
4. KAUFMAN, S., AND SINGLETERRY, C. R., *J. Colloid Sci.* **12**, 465 (1957); KAUFMAN, S., *ibid.* **17**, 231 (1962).
5. HEILWEIL, I. J., *J. Colloid Sci.* **19**, 105 (1964).
6. REERINK, H., *J. Colloid Sci.* **20**, 217 (1965).
7. KITAHARA, A., KOBAYASHI, T., AND TACHIBANA, T., *J. Phys. Chem.* **66**, 363 (1962).
8. FRANK, S. G., AND ZOGRAFI, G., *J. Pharm. Sci.* **58**, 993 (1969).
9. PERI, J. B., *J. Colloid Interface Sci.* **29**, 6 (1969).
10. KON-NO, K., AND KITAHARA, A., *J. Colloid Interface Sci.*, in press.
11. WILLIAMS, E. F., WOODBERRY, N. T., AND DIXON, J. K., *J. Colloid Sci.* **12**, 452 (1957).
12. KON-NO, K., AND KITAHARA, A., *Nippon Kagaku Zasshi* **91**, 539 (1970).
13. KUWAMURA, T., *Kogyo Kagaku Zasshi* **64**, 1958 (1961); KUWAMURA, T., *ibid.* **64**, 1965 (1961).
14. KITAHARA, A., WATANABE, K., KON-NO, K., AND ISHIKAWA, T., *J. Colloid Interface Sci.* **29**, 15 (1969).
15. KON-NO, K., AND KITAHARA, A., *Nippon Kagaku Zasshi* **91**, 328 (1970).
16. KITAHARA, A., *J. Phys. Chem.* **69**, 2788 (1965).
17. SIRIANNI, A. F., COWIE, J. M. G., AND PUDINGTON, I. E., *Can. J. Chem.* **40**, 957 (1962).
18. CORKILL, J. M., GOODMAN, J. F., AND WALKER, T., *Trans. Faraday Soc.* **61**, 589 (1965).
19. LITTLE, R. C., AND SINGLETERRY, C. R., *J. Phys. Chem.* **68**, 3453 (1964).
20. BECHER, P., *J. Phys. Chem.* **64**, 1221 (1960).
21. BECHER, P., in M. J. SCHICK, Ed., "Nonionic SURFACTANTS," pp 511-513. Marcel Dekker, New York, 1967.