Properties of Aqueous Solutions of Several Salts of α,ω-Alkanediol Disulfates

MINORU UENO, SATOSHI YAMAMOTO, and KENJIRO MEGURO, Department of Chemistry,
Science University of Tokyo, Kagurazaka Shinjuku-ku, Tokyo, Japan

ABSTRACT

Several salts of α,ω-sulfates, $MO_3SO(CH_2)_n OSO_3M$(n = 12, 14, 16, 18, and M = Li, Na, and K) were prepared from the corresponding α,ω-alkane diols. The Krafft points of these α,ω-sulfates with common counterion as estimated by electroconductivity measurements increased with the increase of the hydrocarbon chain length, and the effect of the counterions on the Krafft points of the α,ω-sulfates with the same hydrocarbon chain lenght was in the order : Li<Na<K. Solutions of the α,ω-sulfates, except disodium dodecanediol disulfate, showed two break points corresponding to the first and second critical micelle concentraion in each plot of the electroconductivity as a function of the concentration. The existence of the second break point suggested that another aggregation of rearrangement of the existing aggregates occurs in α,ω-sulfate solutions in addition to the usual micelle formation. The first and second break points of α,ω-sulfates with sodium counterion decreased logarithmically with increasing total number of methylene groups. The relationships were given as follows: log(first break point) = -0.138Nc-0.095; log(second break point) = -0.104Nc-0.251. The effect of the counterions upon the break points of α,ω-sulfates with the same hydrocarbon chain length was in accordance with their positions in the lyotropic series.

INTRODUCTION

Micellar properties of aqueous solutions of primary alcohol sulfates have been studied extensively (1). These studies established that both alkyl chain length and counterion conspicuously affect the micelle formation of the sulfates. On the other hand, solution properties of α,ω-alkane dicarboyxlates (2,3) and disulfates (4) recently have been reported. In an earlier article, we have dealt with some properties of aqueous solutions of a series of disodium di-3-sulfopropyl-α,ω-alkane dicarboxylate (5). Those α,ω-type surfactants showed two break points in each plot of electroconductivity as a function of surfactant concentration.

The results were interpreted as indicating the existence of two critical concentrations for micelle formation characteristic of those surfactants.

More recently, we have described the syntheses of a series of disodium salts of α,ω-alkanediol sulfates with 12, 14, 16, and 18 carbon atoms and the determinations of their Krafft points and the critical micelle concentration (cmc) values by the surface tension and electroconductivity methods (6), but, in those days, the second cmc was not observed in the electroconductivity and surface tension curves. Later, careful electroconductivity measurements of those disodium salts in aqueous solutions showed the existence of two break points for the α,ω-sulfates corresponding to their first and second cmc on their electroconductivity curves.

In this article, therefore, an attempt was made to determine two break points of several alkali salts of α,ω-sulfates with 12, 14, 16, and 18 carbon atoms by the electroconductivity method. The effects of alkly chain length and counterions upon the micellar properties of these surfactants are discussed in terms of the carbon atom number and the lyotropic series and counterions size.

EXPERIMENTAL PROCEDURES

Materials

Disodium salts of 1,12-dodecanediol and 1,14-tetradecanediol disulfates ($C_{12}Na$ and $C_{14}Na$); dilithium; disodium and dipotassium salts of 1,15-hexadecanediol disulfates ($C_{16}Li$, $C_{16}Na$ and $C_{16}K$); and dilithium, disodium, and dipotassium salts of 1,18-octadecanediol disulfates ($C_{18}Li$, $C_{18}Na$, and $C_{18}K$) were prepared by the method described previously (6).

Carbon, hydrogen, and sulfur analyses of each series were found to be within ca. 0.3% of the theoretical values as shown in Table I.

Measurements

Krafft point: The Krafft point was taken as the temperature at which there was a rapid increase of the solubility of the surfactant in water when gradually heated. The rapid increase of solubility at the Krafft point was in proportion to the rapid increase in electrical conductivity. Therefore, the measurement of the rapid increase in the conductivity of the surfactant solution with temperature in the presence of sufficient surfactant to give a solid phase made it possible to estimate the Krafft point. A test tube was used as the vessel for measuring conductivity. The surfactant solution (50 ml 50 mmole) and the cell

TABLE I

Elementary Analysis of α,ω-Disulfates

	Carbon		Hydrogen		Sulfur	
α,ω-Disulfates	Found	Calculated	Found	Calculated	Found	Calculated
$C_{12}Na$	36.03	35.46	5.67	5.95	15.66	15.78
$C_{14}Ma$	39.26	38.70	7.00	6.50	14.61	14.76
$C_{16}Li$	44.56	44.65	7.69	7.49	14.64	14.90
$C_{16}Na$	42.28	41.55	7.14	6.97	13.51	13.86
$C_{16}K$	38.82	38.84	6.58	6.51	12.59	12.96
$C_{18}Li$	47.08	47.16	7.85	7.91	13.85	13.99
$C_{18}Na$	44.23	44.23	7.18	7.40	12.65	13.08
$C_{18}K$	41.25	41.35	6.90	6.94	12.25	12.27

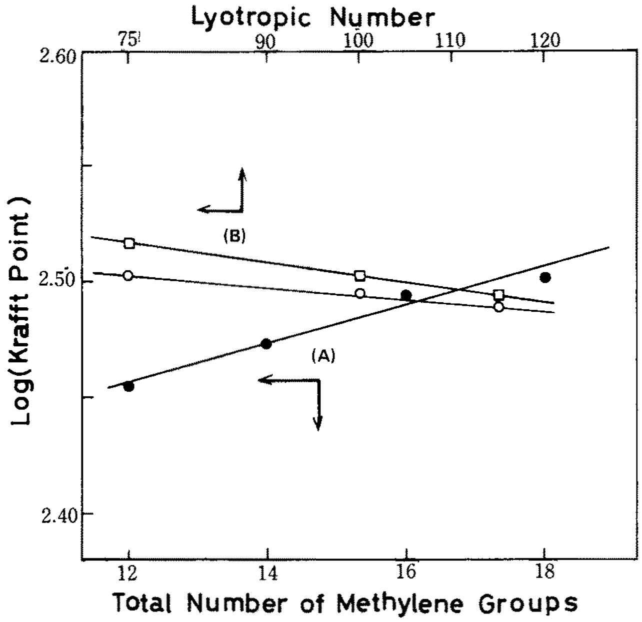

FIG. 1. A. Relationship between log Krafft point and total number of methylene groups in the alkyl chain of disodium α,ω-sulfates (●). B. Relationship between log Krafft point and Lyotropic number of counterions. C_{16} (○) and C_{18} (□).

(electrodes) were placed in the test tube. Then the vessel was immersed in a heating bath. The solution was stirred with a mechanical stirrer, and the temperature was increased at a rate of about 0.1 C/min.

Electroconductivity: The conductivity of solution was measured with a CG20IPL conductivity cell and a no. C68174G conductivity resistivity indicator (Toa Denpa Co.). The cell constant was determined by using 0.001 m potassium chloride solution. All measurements were made in a thermostat controlled at a constant temperature (±0.1 C) above the Krafft point for each member of the series of α,ω-sulfates. The temperatures were at 45 C for $C_{12}Na$ and $C_{14}Na$; 60 C for $C_{16}Li$, $C_{16}Na$, and $C_{16}K$; and 70 C for $C_{18}Li$, $C_{18}Na$, and $C_{18}K$, respectively. The specific conductivity of purified water used was always ca. 1.0×10^{-6} ohm$^{-1}\cdot$cm^{-1} at 25 C.

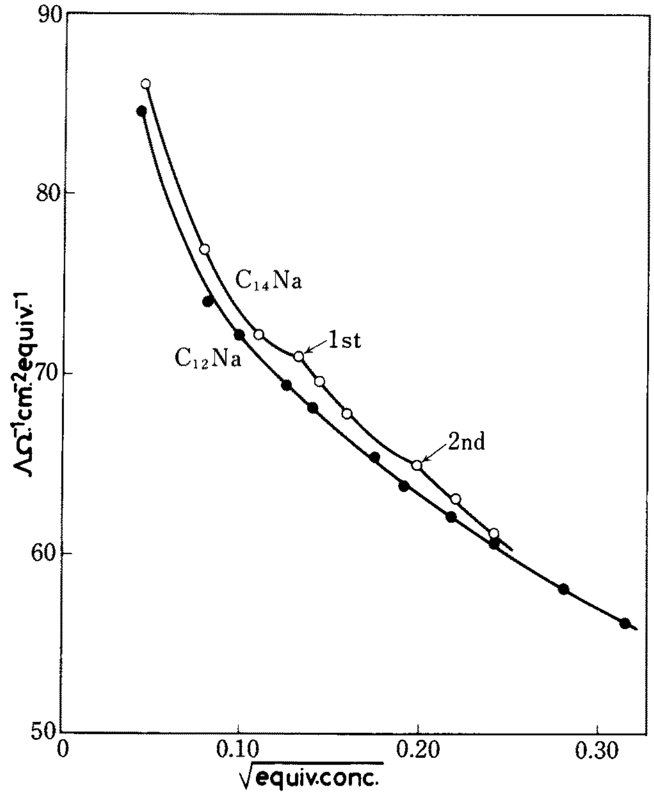

FIG. 2. Equivalent conductivities of disodium 1,12-dodecane sulfate ($C_{12}Na$) and disodium 1,14-tetradecane sulfates ($C_{14}Na$). $C_{12}Na$ (●) and $C_{14}Na$ (○).

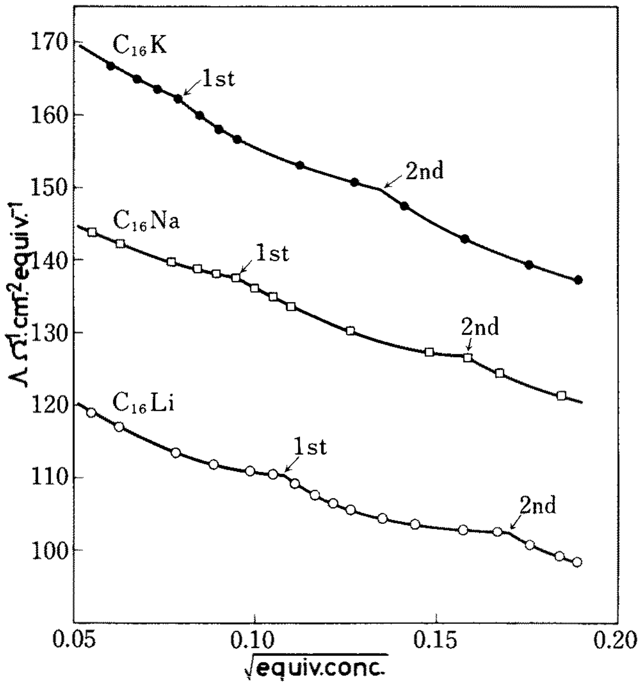

FIG. 3. Equivalent conductivities of alkali salts of 1,16-hexadecane sulfates. $C_{16}Li$ (○), $C_{16}Na$ (□), and $C_{16}K$ (●).

RESULTS AND DISCUSSION

Effects of chain length and counterion on the Krafft point: The characteristic properties of surfactants with methylene groups of different length are conditioned by the sudden great increase of the solubility at the Krafft point (7,8). It is well recognized by many authors that micelles exist only at temperatures above the Krafft point. Therefore, the Krafft point of each member of a series

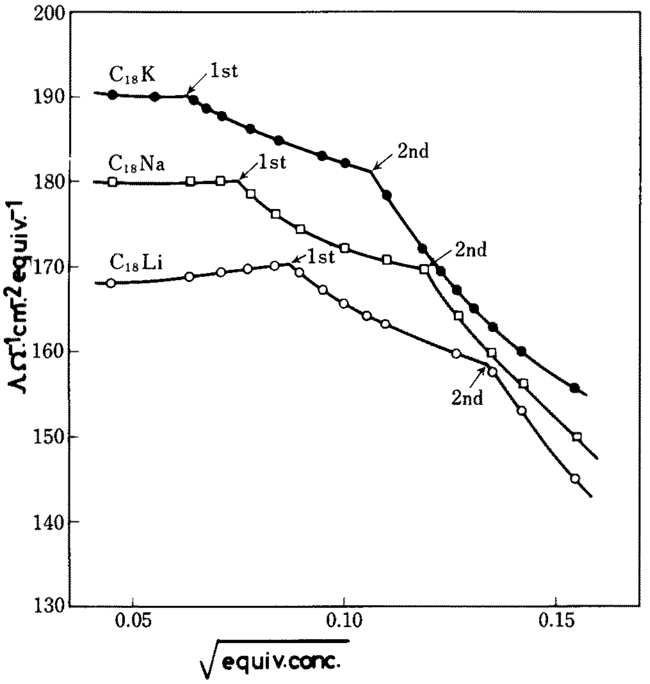

FIG. 4. Equivalent conductivities of alkali salts of 1,18-octadecane sulfates. $C_{18}Li$ (○), $C_{18}Na$ (□), and $C_{18}K$ (●).

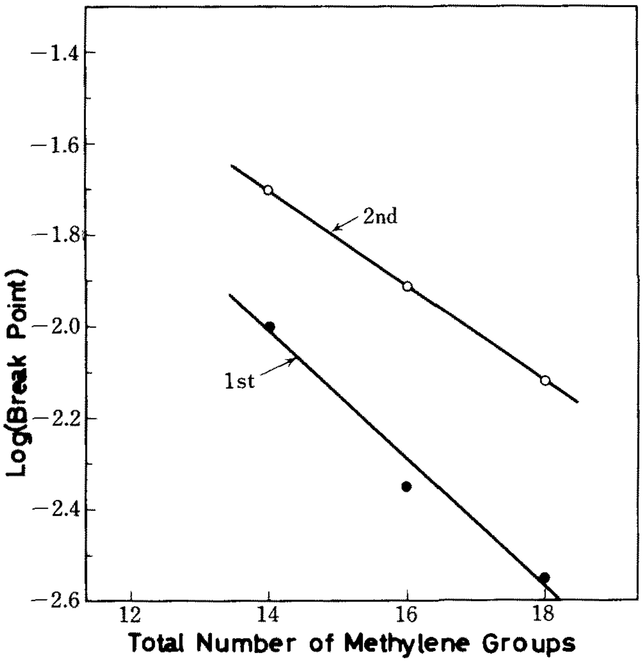

FIG. 5. Relationship between log break point (corresponding to critical micelle concentration) and total number of methylene groups in alkyl chain of disodium α,ω-alkane sulfate. First break point (●). Second break point (○).

of surfactants should be determined before the measurements of electroconductivity and other properties relating to the micelle formation in solutions.

The Krafft points of the α,ω-alkanediol sulfates evaluated from the intersection of two extrapolated straight line portions of the specific conductivity curves are listed in Table II, the last column of which gives the data for alkali salts of alkyl monosulfates (9) for comparison.

The Krafft points of the α,ω-sulfates with common counterion increased with the increase of hydrocarbon chain length as shown in Figure 1A.

This figure also gives a similar behavior of monosulfates (9). However, the values for the α,ω-sulfates are lower than those of the corresponding alkyl monosulfates with the same chain length. The lowering may be due to their chemical structure with polar head groups at both ends of a long alkyl chain.

The effectiveness of the three counterions, Li, Na, and K, in reducing the Krafft points of both C_{16} and C_{18} disulfates is in accordance with their order in the lyotropic series, as is evident from Table II, i.e. with the increasing order of the size of hydrated ions. This order of the effectiveness of the counterions in lowering the Krafft points of the α,ω-sulfates is depicted in Figure 1B. Large hydrated ions (high lyotropic number) are more effective in solubilizing the α,ω-sulfates into water than small hydrated ions (low lyotropic number).

Effects of alkyl chain length and counterion on two break points: The results on the electroconductivity are shown in Figures 2, 3, and 4, in which the equivalent conductivity is plotted against the square root of equivalent concentration. With the exception of $C_{12}Na$, all other salts showed two distinct break points in dilute and concentrated regions of their electroconductivity curves, respectively. In the case of $C_{12}Na$, no break point corresponding to the cmc was found over the whole region of the curve. The values of concentrations at two break points are listed in Table III.

The data in the last column of the Table are for sodium salts of alkyl monosulfates (10,11) for comparison.

This feature has not been observed before and is certainly not seen for ordinary surfactants. The first break

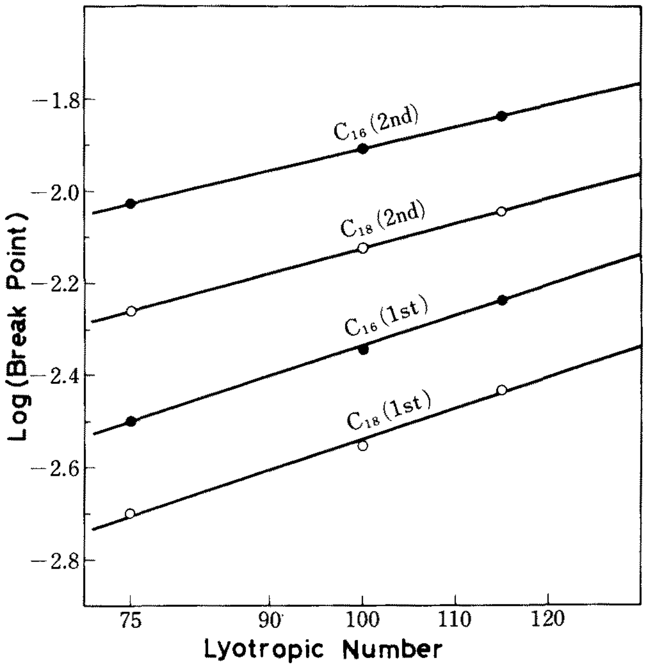

FIG. 6. Relationship between log break point (corresponding to critical micelle concentation) and lyotropic number of counterion. C_{16} (●) and C_{18} (○).

points for disodium salts of the α,ω-sulfates determined by the electroconductivity method are close to those obtained previously from surface tension measurements (6), which give only one break point corresponding to the first cmc, and so the values of concentrations at first break point can be regarded as the usual cmc.

On the other hand, the second break point may be brought about by introduction of a second polar group into the structure of normal type of surfactant, and it may permit the size and shape of the micelles to change in the electrical properties of the solutes, since no appreciable change in surface tension is detected.

When the values of the first and second break points are logarithmically plotted against the number of carbon atoms (Nc) in the alkyl chain for both break points of the α,ω-sulfates with sodium as their counterion, a linear relationship can be found, as shown in Figure 5. The relationships are expressed by the following equations:

$$\log(\text{first break point}) = -0.138\text{Nc} - 0.095 \quad \text{(I)}$$
$$\log(\text{second break point}) = -0.104\text{Nc} - 0.251 \quad \text{(II)}.$$

It is interesting to note here that the numerical factors 0.138 and 0.104 of Nc in equations I and II are ca. one-half to one-third of the values of 0.29 for the usual monosulfates (12).

In general, in accordance with this logarithmic relation between the cmc and the number of carbon atoms or CH_2

TABLE II

Krafft Points of α,ω-Sulfates and Alkyl Monosulfates (9)

Carbon atoms	Counterion[a]	α,ω-Sulfates	Monosulfates
8	Na	---	---
10	Na	---	8
12	Na	12	21
14	Na	24.8	35.8
	Li	35	---
16	Na	39.1	43.0
	K	45.0	---
	Li	39.0	---
18	Na	44.9	57.5
	K	55.0	---

[a] Lyotropic number of alkali cations: Na = 100, Li = 115, and K = 75.

TABLE III

Values of Concentrations at Break Points of Various Salts of α,ω-Sulfates and Sodium Salts of Alkyl Monosulfates (9,10) from Electroconductivity Data

		α,ω-Disulfates			Monosulfates	
Carbon atoms	Counterion[a]	First break points (mM 1^{-i})	Second break points (mM 1^{-i})	Temperature C	CMC[b] (mM 1^{-i})	Temperature C
8	Na	---	---	---	136	40
10	Na	---	---	---	31	25
12	Na	---	---	45	8.65	40
14	Na	10.0	20.0	45	2.4	40
	Li	5.8	14.5	60	---	---
16	Na	4.5	12.4	60	0.58	40
	K	3.2	9.4	60	---	---
	Li	3.7	9.0	70	---	---
18	Na	2.8	7.6	70	0.165	40
	K	2.0	5.5	70	---	---

[a] Lyotropic number of alkali cations: Na = 100, Li = 115, and K = 75.

[b] CMC = critical micelle concentration.

groups, the energy required to transfer a surfactant molecule from a hydrocarbon environment to water has been found to increase by a definite amount for each additional CH_2 group in the hydrocarbon chain (12), and the magnitude of the energy for a carbon atom of CH_2 group is ca. proportional to the factor of Nc in Equation I and II, and so the micelle formation of the α,ω-sulfates, compared to that of monosulfates with the same hydrocarbon chain length, may become difficult. This is evident from the values of the break points of the α,ω-sulfates in Table III, indicating that the values of the first break point with sodium ion are larger than those of sodium monosulfates with same hydrocarbon chain length.

The α,ω-sulfates have a molecular structure equivalent to the alkyl parts of two molecules of monosulfates of one-half the alkyl chain length being joined. Accordingly, the α,ω-sulfates may be expected to show surface properties intermediate between those of the monosulfates with one-half the chain length of the corresponding α,ω-sulfates, and the monosulfates with the same chain length as the corresponding α,ω-sulfates.

The alkyl monosulfates with the carbon number below ca. 8 behave as uniunivalent simple electrolyte salt in aqueous solution, and, hence, the micell formation of these monosulfates becomes difficult. However, when two molecules of a monosulfate with the carbon number ca. 7 connect together to make a molecule, such as α,ω-sulfate, micelle formation of the α,ω-sulfate may occur more easily than that of the alkyl monosulfate, because the degree of freedom for the kinetic motion of α,ω-sulfate in the solution is resticted. On the other hand, the hydrophilic polar groups at both ends of alkyl chain of the α,ω-sulfates make it more difficult to form micelles than the alkyl monosulfates having the same chain length.

The effect of counterions on both the first and second break points of the two α,ω-sulfates with 16 and 18 carbon atoms is found to be a function of lyotropic number. A considerable increase in the values of two break points is observed with the increase in lyotropic number, as is evident from Figure 6.

Thus, the counterion with the lowest lyotropic number (small hydrated ion) brings about the largest decrease in the break point and vice versa.

TABLE IV

Ionic and Hydrated Radii for Counter Ions

Alkali metal ion	Ionic radius (Å)	Hydrated radius (Å)
Li	0.60	3.82
Na	0.95	3.58
Ka	1.33	3.31

The effectiveness in decreasing the break points of the two α,ω-sulfates is in the order: K>Na>Li. This was in the same order as observed by Goddard, et al. (13).

This is in accordance with their positions in the lyotropic series (Table II). The lowering in the break points in the case of the two α,ω-sulfates can be explained in terms of the hydration of counterions. It has been suggested (14) that, in aqueous solutions, the extent of the counterions' interaction with water is an important factor in determining the relative aggregating power of surfactants with the same alkyl chain. Nightingale (15) gave the data in Table IV for alkali ions.

As pointed out by Mukerjee (16,17), since the hydration of counterions is scarcely lost during micellization, the size of hydrated ions would be important in the micelle formation. Mukerjee and coworkers (18) claimed that, the larger the size of the hydrated ion, the less closely it can approach the charged surface of the micelle to reduce its charge. Thus, the most heavily hydrated Li ion cannot approach the micellar surface so closely and is not so effective, therefore, in screening the charge on the ionized groups of the micelle. A greater electrostatic barrier has to be overcome on micellization, and this is reflected in the higher values of the break points.

REFERENCES

1. Kling, W., and H. Lange, "Second International Congress of Surface Activity, 1957," Butter Worths Scientific Publications, London, England, p. 295.
2. Danielson, I., Acta Acad. Aboensis Math. Phys. 20:7 (1956).
3. Elworthy, P.H., J. Pharm. Pharmcol. 11:557 (1959).
4. Elworthy, P.H., Ibid. 11:624 (1959).
5. Ueno, M., T. Hikota, T. Mitamura, and K. Meguro, JAOCS 49:250 (1972).
6. Meguro, K., M. Ueno, Y. Asano, M. Kawanabe, and S. Yamamoto, "Fifth International Congress of Surface Activity, 1958," Ediciones Unidas, S.A., Barcelona, Spain, p. 815.
7. Tartar, H.V., and K.A. Wright, J. Amer. Chem. Soc. 61:539 (1939).
8. Shinoda, K., and T. Soda, J. Phys. Chem., 67:2072 (1963).
9. Raison, M., "Second International Congress of Surface Activity, 1957," Butter Worths, Scientific Publications, London, England, p. 422.
10. Shinoda, K., T. Nakagawa, B. Tamamushi, and T. Isemura, "Colloidal Surfactants, Academic Press, New York, N.Y., 1963, p. 48.
11. Haffner, F.D., G.A. Piccione, and C. Rosenblum, J. Phys. Chem. 46:662 (1942).
12. Klevens, H.B., JAOCS 30:74 (1953).
13. Goddard, E.D., O. Harva, and T.G. Jones, Trans. Faraday Soc. 49:980 (1953).
14. Anacker, E., J. Phys. Chem. 67:1713 (1963).
15. Nightingale, E., Ibid. 63:1381 (1959).
16. Mukerjee, P., Ibid. 66:943 (1962).
17. Mukerjee, P., J. Colloid Sci. 19:722 (1964).
18. Mukerjee, P., Mysels, K., and Paz Papauan, P., J. Phys. Chem., 71:4166 (1967).

[Received February 1, 1974]