The Effect of Temperature on Micelle Formation and Solubilization in Benzene

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Introduction

There have been recently some reports on micelle formation[1,2,3] and solubilization[4,5,6,7] in a *non-polar solvent*. Since, however, detergents used are limited and the concentration dependence of solubilization has scarcely ever been obtained[8], more experimental data seem to be necessary in order to clarify the general behavior of detergents in a *non-polar solvent*.

The present author[9] has already discussed the micelle formation from the standpoint of the relation between the van't Hoff factor and the concentration of a detergent and

1) L. Arkin and C.R. Singleterry, *J. Am. Chem. Soc.*, **70**, 3965 (1948).
2) S. Kaufman and C.R. Singleterry, *J. Colloid Sci.*, **7**, 453 (1952).
3) M. van der Waarden, *J. Colloid Sci.*, **5**, 448 (1950).
4) L. Arkin and C.R. Singleterry, *J. Colloid Sci.*, **4**, 537 (1949).
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6) S.R. Palit and J.W. McBain, *J. Chem. Soc. Ind.*, **66**, 3 (1947).
7) S.R. Palit and V. Venkateswarlu, *Proc. Roy. Soc.*, **A208**, 542 (1951).
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9) A. Kitahara, *This Bulletin*, **28**, 234 (1955).

from the standpoint of the change of the maximum amount of water solubilized under varying concentration of detergents in benzene including a series of pure fatty acid salts of amines.

In this paper, the van't Hoff factor and the maximum amount of water solubilized are measured under varying concentrations and temperatures in benzene for the above materials. In this connection a few reports[3,7,10] on the temperature dependence of solubilization are also available, but a conclusive result has not yet been obtained.

Experimental

Materials.—Dodecylammonium propionate, butyrate, caproate, caprylate and caprate, and octadecylammonium propionate and butyrate were used as detergents. The preparation of detergents was similar to that already reported[9]. They were all white crystalline and had definite melting points within the range of ±1°C. It was suggested from their infrared spectra that their structures are ion pairs of $[RCOO^-]\,[H_3NR']^+$. Benzene and water were purified as usual.

Precedures.—Van't Hoff factors of these detergents in benzene were determined at different concentrations cryoscopically and ebullioscopically. Cryoscopy was carried out by means of the usual Beckmann's apparatus, and ebullioscopy by the revised Cottrell's apparatus[11].

A maximum amount of water solubilized in a benzene solution of a detergent was determined at various concentrations as in the preceding paper[9]. The occurrence of turbidity which determines the limit of solubilization was sharp with the change of the amount of added water for caproate, caprylate and caprate of both amines, though not relatively sharp for propionate and butyrate. The turbidity was a faintly milky state in the later cases and an assembly of very small droplets in the former cases. The measurements were carried out at 10°, 26° and 40°C in an air thermostat. The fluctuation of temperature was ±1°C.

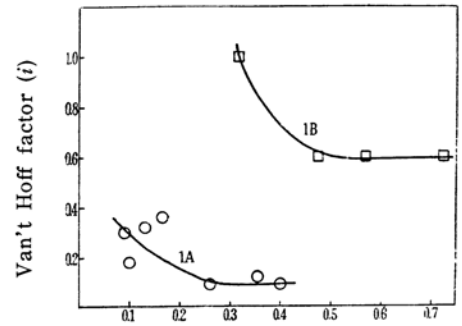
Result and Discussion

The Effect of Temperature on Micelle Formation.—The results of cryoscopy and ebullioscopy are given in Figs. 1, 2 and 3 for dodecylammonium propionate, caproate and caprylate, respectively. The ordinate shows the van't Hoff factor (i) and the absissa the square root of the molality of detergents.

The values of van't Hoff factors were larger than 1.0 in the lower range of concentrations, and this concentration range is higher in the case of ebullioscopic result than in the case of cryoscopic one. These values, however, were not shown in these figures. This seems to show that the detergent molecule decomposes as follows:

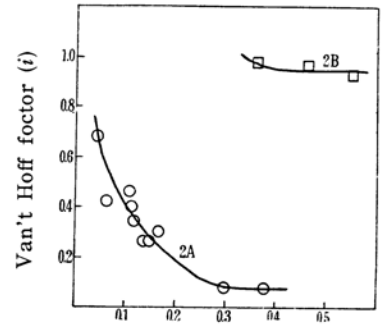
$$[RCOO^-]\,[H_3NR']^+ \rightarrow RCOOH + R'NH_2.$$

This is also suggested from the following



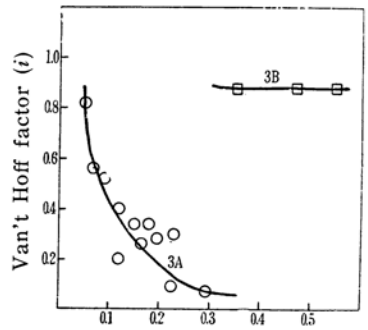
Square root of molality

Fig. 1. The relation between the van't Hoff factor and the molality of dodecylammonium propionate.
1A: at melting point
1B: at boiling point



Square root of molality

Fig. 2. The relation between the van't Hoff factor and the molality of dodecylammonium caproate.
2A: at melting point
2B: at boiling point



Square root of molality

Fig. 3. The relation between the van't Hoff factor and the molality of dodecylammonium caprylate.
3A: at melting point
3B: at boiling point

10) P. A. Winsor, *Trans. Faraday Soc.*, **44**, 455 (1948).
11) H. Shiba and T. Imase, *Sci. Paper Inst. Phys. Chem. Res.*, **7**, 996 (1928).

infrared spectroscopic observation. The infrared spectra of dodecylammonium caprylate in carbon tetrachloride shows an absorption peak at 1753 cm^{-1} in the concentration of 0.0046 mol./l. at room temperature. This peak is attributed to a carbonyl group of a free acid. In the concentration of 0.096 mol./l. this peak becomes very weak. It is expected that decomposition process will take place up to the relative high concentrations at a high temperature, but it will do only in the lower ones at a low temperature.

The curves of the relation between i and the concentration obtained from the cryoscopic method (1A, 2A and 3A) show a steep decrease at a certain range of concentration while at the higher concentration the values of i were markedly reduced, indicating the formation of large aggregates. On the other hand, different from the case of the melting temperature, the curves 2B and 3B which were obtained from ebullioscopy show only a very slight decrease in i over a wide range of the concentrations. The curve 1B shows apparently a moderate decrease, but since the values of i are still very much larger than those of 1A, it can be seen that the average degree of aggregation is very much smaller.

The above comparison clearly shows the effect of temperature on micelle formation, though we cannot know the precise behavior at temperatures between the melting point and the boiling point. It is evident from Figs. 1, 2 and 3 that at a low temperature (5°C), micelle formation begins to take place at a certain concentration, but at a high temperature (80°C) slight or no micelle formation takes place at least within the concentration range of the present experiment.

The Effect of Temperature on Solubilization.—The relation between the maximum amount of water solubilized (S) and the concentration of a detergent at 10°, 26° and 40°C was plotted in Figs. 4, 5 and 6, respectively. The ordinate shows the S in molality and the absissa the molality of a detergent. At 10°C the fairly slight solubility made the experiment of solubilization impossible for dodecylammonium caprate, octadecyl-

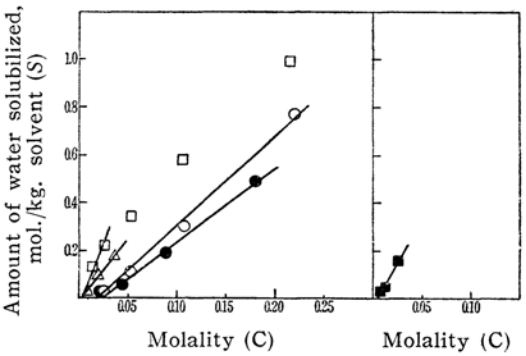


Fig. 4.
The relation between the amount of water solubilized and the molality of detergent at 10°C.
△ Dodecylammonium propionate
□ Dodecylammonium butyrate
○ Dodecylammonium caproate
● Dodecylammonium caprylate
◐ Dodecylammonium caprate
▲ Octadecylammonium propionat
■ Octadecylammonium butyrate

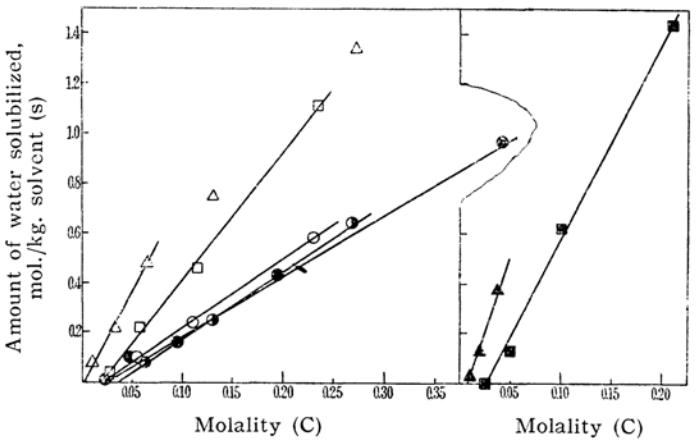


Fig. 5.
The relation between the amount of water solubilized and the molality of detergent at 26°C.
△ Dedocylammonium propionate
□ Dodecylammonium butyrate
○ Dodecylammonium caproate
● Dodecylammonium caprylate
◑ Dodecylammonium caprate
▲ Octadecylammonium propionate
■ Octadecylammonium butyrate

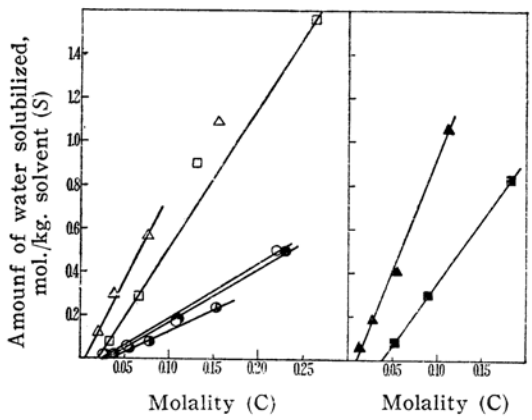


Fig. 6.
The relation between the amount of water solubilized and the molality of detergent at 40°C.
△ Dodecylammonium propionate
□ Dodecylammonium butyrate
○ Dodecylammonium caproate
● Dodecylammonium caprylate
◑ Dodecylammonium caprate
▲ Octadecylammonium propionate
■ Octadecylammonium butyrate

ammonium propionate and higher concentrations of dodecylammonium propionate. The experimental error of the S was ± 0.01 and ± 0.02 in molality at the lower and the higher S, respectively. The marks of circles, triangles and tetragons in Figs. 4, 5 and 6 were drawn somewhat larger than the range of the experimental error.

It is evident within the experimental accuracy that the $S\sim$concentration relation is linear within the concentration range of this experiment, excepting the cases of higher concentrations of dodecylammonium butyrate and probably propionate at 10°C and the cases of dodecylammonium propionate at 26°C and 40°C. That is,

$$S=\alpha(C-\beta),$$

where, C=the concentration of a detergent (molality), α, β=constants.
The value of α is referred to as the solubilizing power, and the value of β may be called the apparent critical micelle concentration obtained from solubilization.

Pink[8] has also observed this linearity, but the straight line passed the origin of the concentration. Provided that the detergent micelle is monodisperse, the value of S should be proportional to the micellar concentration. Singleterry et al.[2] have reported that the micellar concentration is proportional to the total concentration of a detergent above a critical range. Thus it will be said that the linearity, which was obtained experimentally between the S and the total concentration of a detergent, is an evidence for the monodispersity of the micellar size and shape.

However, the existence of the critical micelle concentration in a non-polar solvent may be open to discussion. Singleterry et al.[1,2] determined the critical micelle concentration of Ca-xenylstearate in benzene with use of the fluorescent dye. Since it has been found that the existence of water changes the size and shape of micelles[4], the question arises whether the critical micelle concentration is determined by the extrapolation of the relation between the amount of the solubilizate and the concentration of a detergent in a non-polar solvent as in an aqueous one. But in this experiment the effect of water on the fluidity of a solution was not qualitatively observed as in that paper[4]. Further, it is said that the effect of water on the size and shape of soap micelles disappears when the amount of water exceeds about two moles per one mole of a soap[4]. The amount of water solubilized in this experiment exceeds this value in every case, as seen from values of α of Table I. It might be, therefore, assumed that water solubilized does not affect the size and shape of micelles. Hence, the apparent critical micelle concentration was reasonably obtained by the extrapolation of the above linear relation.

The valves of α and β obtained graphically from Figs. 4, 5 and 6 are given in Table I. In the exceptional non-linear cases the formula can be applied in the lower concentration range, and the constants α and β can be similarly obtained. The values of β may not be sufficient for the quantitative discussion, considering from the standpoint of experimental accuracy. But the following qualitative conclusions are drawn from Table I.

TABLE I
CRITICAL MICELLE CONCENTRATION (c.m.c.) AND SOLUBILIZING POWER AT DIFFERENT TEMPERATURE

Temperature (°C)	β: c.m.c. (mol./kg. solvent) 10	26	40	α: Solubilizing power 10	26	40
Dodecylammonium propionate	0.002	0.002	0,005	5.7	7.2	8.0
〃 butyrate	0.003	0.018	0.020	9.4	4.6	9.2
〃 caproate	0.018	0.020	0.025	3.7	2.9	2.5
〃 caprylate	0.020	0.025	0.025	3.0	2.8	2.5
〃 caprate	—	0.035	0.032	—	2.9	2.1
Octadecylammonium propionate	—	0.008	0 010	—	12	10
〃 butyrate	0.005	0.027	0.028	8.0	9.0	5.7

At constant temperature the value of α decreases and that of β increases with the increase of the carbon number. The increase of β corresponds to the experimental result obtained by Pink et al.[12] They have reported that the number of molecules in the micelle decreases with increase in the length of the hydrocarbon chain in the case of a metal soap in toluene, though the value is an extrapolated one to infinite dilution at boiling temperature.

Rise of temperature decreases the solubilizing power except for the case of propionate and butyrate[13] and increases the critical micelle concentration. The following qualitative experiment was further carried out in order to ascertain the effect of temperature on solubilization. The value of S for benzene solutions of dodecylammonium propionate, caproate and caprylate was determined at 74°C. The amount was corrected for the solubility of water into benzene at the temperature. The corrected value was given in the 3rd column in Table II. Next, a certain amount of water was added to those solutions at 25°C, and the turbidity was observed (4th and 5th columns). Then these solutions were brought and left to stand with occasional shaking in a bath of the temperature varied in the order of 40°, 25°, 10°C and then in the reverse order. Thus the turbidity was observed at each temperature. The results were independent of the direction of temperature change, and were listed in Table II.

Relation between Micelle Formation and Solubilization. — The following facts are noticed in Table II. A benzene solution of the detergents solubilizes scarcely any water near the boiling point (74°C), though a concentrated solution of dodecylammonium propionate seems to solubilize a slight amount of water. The solution has a tendency to solubilize a certain amount of water, when the temperature is lowered. Slight or no solubilization near the boiling point and the marked increase at a lower temperature correspond to the values of higher and lower van't Hoff factors at boiling and melting temperature, respectively. It is noticeable that in the case of dodecylammonium propionate the temperature dependence is reversed between 40°C and 74°C.

Summary

Van't Hoff factors of fatty acid salts of higher aliphatic primary amines in benzene were determined cryoscopically and ebullioscopically. Slight or no micelle formation takes place at boiling temperature, though it does take place at melting temperature.

Solubilization of water into benzene by these detergents was measured at 10°, 26° and 40°C. With rise of temperature the critical micelle concentration obtained from solubilization increases and the solubilizing power decreases, though the solubilizing power of propionate and butyrate shows an anomaly. Solubilization and micelle formation determined here change parallel to each other with varying temperature.

Table II

The effect oe temperature on solubilization

Detergent	Concentration (molality)	Maximum amount of water solubilized at 74°C (molality)	Amount of water added at 25°C (molality)	Turbidity 25° ⇄ 40° ⇄ 25° ⇄ 10°			
Dodecylammonium propionate	0.174	0.05±0.02	0.91	+	−	+	++
	0.085	0.04±0·02	0.52	±	−	±	++
Dodecylammonium caproate	0.289	0.04±0.03	0.71	−	±	−	−
	0.140	0.00	0.31	−	++	−	−
Dodecylammonium caprylate	0.204	0.00	0.42	−	++	−	−
	0.095	0.00	0.17	++	++	++	+

++.....strongly turbid, +.....turbid, ±.....faintly turbid, −.....clear.

It is seen from Table II that the rise of temperature decreases solubilization of dodecylammonium caproate and caprylate while it promotes solubilization of dodecylammonium propionate in the range of temperature from 10° to 40°C, which are in accord with the values of the solubilizing power of Table I.

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12) S.M. Nelson and R.C. Pink, *J. Chem. Soc.*, 1952, 1744.

13) Palit et al.[7] report that the solubilizing power at a definite concentration of dodecylammonium butyrate in toluene increases with rise of temperature ranging from 0° to 40°C.