Micelle Formation and Solubilization in Benzene by Fatty Acid Salts of Higher Amines

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Introduction

Whilst numerous investigations have been made on the micelle formation as well as the solubilization both of which take place in *aqueous solutions* of detergents, little is known about the similar phenomena in *non-aqueous solutions.*

Some investigators[1,2] have assumed the micelle formation of detergents in non-polar solvents. However,it is not necessarily certain that detergent molecules can aggregate to micelles spontaneously when they are dissolved in non-polar solvents, because the present theories regarding the micelle formation in aqueous solutions of detergents can not be applied to a case when a solvent is a non-polar one. Hence, the more experimental

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[1] M. van der Waarden, *J. Colloid Sci.*, 5, 448 (1950). S. Kaufmann and C. R. Singleterry, *J. Colloid Sci.*, 7, 453 (1952). M.B. Mathews and E. Hirschhorn, *J. Colloid Sci.*, 8, 86 (1953).

[2] Recently, Palit et al. have observed the enhancement in dissolving power for water into non-polar solvent with the presence of detergent such as fatty acid salts of higher amines, and this apparent solubilization was assumed to be parallel phenomena with micelle formation. See: S. R. Ralit and V. Venkateswarlu, *Proc. Roy. Soc.*, A208, 542 (1951); *J. Chem. Soc.*, 1954, 2129.

evidences are desired concerning the micelle formation as well as the solubilization which may take place in non-aqueous solutions of detergents, especially when the solvents are non-polar ones.

Experimental

Preparation of Detergents.—It was presumed that fatty acid salts of higher aliphatic amines are the most favourable materials as detergents for the present purpose. A series of compounds were prepared in possibly purified states in the following way.

Commercial dodecylamine and octadecylamine were purified by distillation under reduced pressure. The fraction having b.p. 131–133°C under 15 mmHg and those having b.p. 188–190°C under 4 mmHg were collected. Commercial propionic and butylic acid were dried by means of anhydrous copper sulfate and purified by distillation. For the other fatty acids, the products of Nihon Yushi Co. were used. The neutralization of amines with acids was carried out at room temperature. The solvents used in the preparation and the melting points of the products are summarized in Table I.

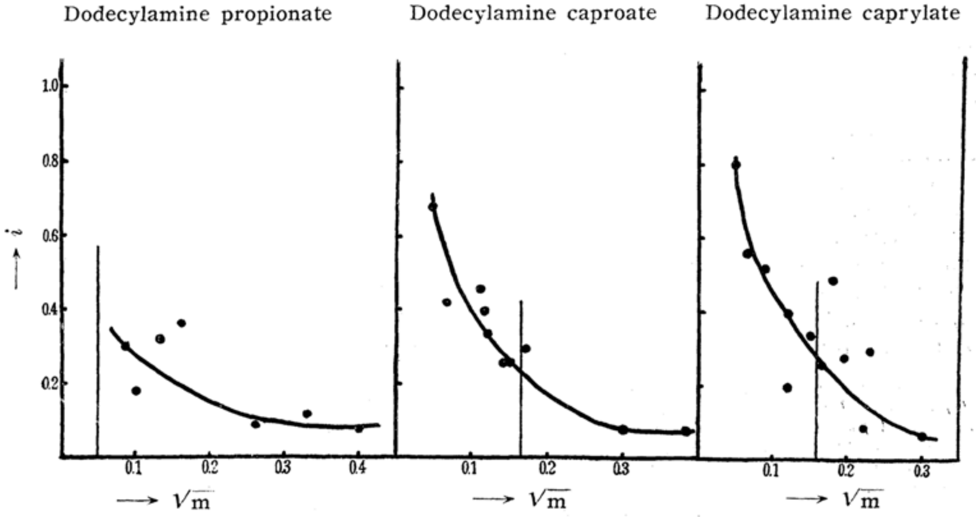
All the purified compounds were white and crystalline. The fluctuation of their melting points was ±1°C. Butylate and caproate of dodecylamine were strongly hygroscopic.

When the reaction of amines and acids was carried out at about 150°C instead of room temperature, substances having different melting points were obtained. The infra-red absorption spectra of reaction products from dodecylamine and propionic acid or capric acid were taken in nujol on a Perkin-Elmer 112 instrument. The products (1) obtained at high temperature showed absorptions at 1630 and 3300 cm^{-1}. The former absorption is attributed to the carbonyl group of

TABLE I

PREPARATION AND MELTING POINTS OF DETERGENTS

Detergent	Solvent used in neutralization	Solvent used in recrystallization	m.p. °C
Dodecylamine propionate	Benzene and *n*-Hexane	—	54–56
„ butylate	*n*-Hexane	*n*-Hexane	39–41
„ caproate	„	„	31–33
„ caprylate	„	—	43–45
„ capriate	Benzine	*n*-Hexane	60–61
„ laurate	„	„	62–64
„ myristate	„	„	64
„ palmitate	„	„	70–71
Octadecylamine propionate	Acetone	Benzine+Acetone	69–72
„ butylate	„	Benzine	56–58
„ caproate	„	„	46–47
„ caprylate	„	Acetone	52–54
„ capriate	„	„	59–61
„ laurate	„	„	62–64
„ myristate	„	—	71–72
„ palmitate	„	—	78–79


Dodecylamine propionate

Dodecylamine caproate

Dodecylamine caprylate

Fig. 1. Change of van't Hoff factor (*i*) with molality (*m*).

acid amide and the latter to its amide group. On the other hand, the corresponding products (2) obtained at room temperature had absorptions at 1400 and 1600 cm^{-1}. These two absorption peaks are attributed to carboxylic ions. Therefore, compounds (1) are acid amides, and (2) are fatty acid salts of higher amines having the structure of $[RCOO^-]$ $[H^+{}_3NR']$[3].

Determination of van't Hoff Factors.—For the purpose of ascertaining micelle formation, the van't Hoff factors (i) for dodecylamine propionate, caproate and caprylate in benzene were determined at various concentrations by means of cryoscopy (Fig. 1). The measurement was carried out with the usual Beckmann's apparatus.

Measurements of Solubilization.—The limiting amount of solubilized water into a benzene solution of a detergent was determined by the following simple method. Five cc. of solution was put into a test tube. By means of a micro-burette, water was added in portions of 0.002–0.003 cc. After addition of each portion the solution was vigorously shaken 50–250 times, and then put to stand for half an hour. The occurrence of turbidity was detected by means of Tyndall light. Near the limit of solubilization, Tyndall light was observed one or two days after water had been added in order to ascertain the attainment of equilibrium. The limit of solubilization was confirmed by the occurrence of faint turbidity. The measurements were carried out at 26°C.

Results and Discussion

Formation of Micelle.—The relation between the van't Hoff factor (i) and the root of molality was given in Fig. 1. At these concentrations the depression of temperature was insufficient to be observed accurately by a Beckmann's thermometer. Accordingly the data are not so accurate and show fluctuation. But these are adequate for qualitative discussion.

In aqueous solutions the critical concentration of micelle formation of ionic detergents has been discussed from the relation between an osmotic coefficient and a concentration.[4] In non-polar solvents micelle formation may be discussed with van't Hoff factor in place of an osmotic coefficient, because an ionic dissociation in non-polar solvent is doubtful. Therefore, Fig. 1 will be useful for the discussion of micelle formation in benzene.

In the cases of dodecylamine caproate and caprylate, the van't Hoff factors show a remarkable decrease at a range of the concentration in the manner similar to the well-known cases of osmotic coefficients in aqueous solutions. It is thought that this remarkable decrease shows the initiation of micelle formation at this range. In the case of dodecylamine propionate, the remarkable decrease was not observed within the concentration range of this experiment. Its range of the initiation of micelle formation seems to be in the left side of the obtained curve, but in this range no measurement was accurately carried out because of the slight depression of temperature. In any case the values of i at higher concentration are sufficient to show that micelles have been formed. It will be, therefore, concluded that micelle formation begins to take place at a certain concentration for these detergents. The phenomenon of solubilization should take place as the result of micelle formation.

On the other hand, the van't Hoff factors of acid amides in benzene have shown only slight decreases at comparable concentrations. For example, van't Hoff factors of dodecyl amide of caproic acid was 1.0 and 0.55 at 0.20 and 0.32 of $\sqrt{m}$, respectively. It is, therefore, assumed that micelles have not been formed at these concentrations in the case of acid amides.

Solubilization of Water.—The amount of solubilized water was plotted against the concentration of detergents, correction being made with respect to the solubility of water in benzene (Figs. 2 and 3). The salts of

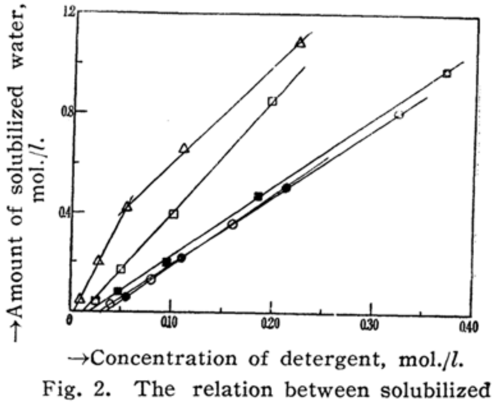


Fig. 2. The relation between solubilized water and concentration of salts of dodecylamine.

- △ dodecylamine propionate
- □ " butylate
- ■ " caproate
- ○ " caprylate
- ● " capriate

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[3] Fatty acid salts of amines and acid amides were prepared, (a) keeping R'=12 and changing R from 3, 4, 6, 8, ..., 16, and (b) keeping R'=18 and R in the same way. It was found that the caproates (R=6) both of (a) and (b) have the lowest melting points in the case of fatty acid salts of amines.

[4] J. W. McBain, "Colloid Science", D. C. Heath & Co., Boston, (1950), p. 242.

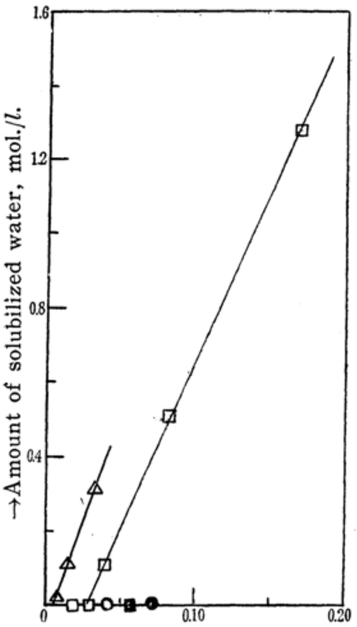

Fig. 3. The relation between solubilized water and concentration of salts of octadecylamine.

△ octadecylamine propionate
□ " butylate
■ " caproate
○ " caprylate
● " capriate

octadecylamine had less solubility as compared with those of dodecylamine. It was, therefore, hardly possible to carry out the measurement at higher concentrations similar to the later case. In octadecylamine caproate, caprylate and capriate, no solubilization was observed even at the concentrations 0.055, 0.040 and 0.077 mol./l., respectively. The measurements on laurate, myristate and palmitate of dodecylamine as well as on those of octadecylamine were impossible because of their limited solubility in benzene. The acid amides, i.e. the reaction products at higher temperature, showed no solubilization at comparable concentrations, corresponding to the slight variance of the van't Hoff factor.

The amount of solubilized water was found to be proportional to the concentration of detergents except for the higher concentration range of dodecylamine propionate. In the concentration range 0.005 – 0.4 mol./l. the relation can be expressed by the formula

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

where, S=amount of solubilized water, mol./l.,
C=concentration of detergents, mol./l.,
α, β=constants.

The values of α and β are given in Table II.

Table II

Values of α and β

Detergent		α	β(mol./l.)
Dodecylamine	propionate	7.2	0.002
"	butylate	4.6	0.012
"	caproate	2.9	0.020
"	caprylate	2.8	0.030
"	capriate	2.9	0.035
Octadecylamine	propionate	12	0.005
"	butylate	9.0	0.028
"	caproate	—	>0.055
"	caprylate	—	>0.040
"	capriate	—	>0.070

The value of α is taken as a measure of solubilizing power, i.e. the number of moles of water which is solubilized per one mole of a detergent. The value of β gives the critical micelle concentration which is obtained from the measurement of the solubilization of water.

From the curve of Fig. 1 a critical concentration of micelle formation cannot be sharply recognized. But it is seen from the comparison between the values of β and Fig. 1 that the value of the critical micelle concentration from the data of solubilization (the value of β) is within the steep range of decreasing in the curve. The vertical lines of Fig. 1 show the values of β, the unit of concentration being corrected. It will be, therefore, concluded that the idea of micelle formation which is suggested from the cryoscopical experiment is not in conflict with that of micelle formation from solubilization.

It is seen from Table II that the critical micelle concentration increases with the chain length of the acid part as well as of the amine part and that the small critical micelle concentration corresponds to the great solubilizing power. The relation between the critical micelle concentration and the chain length is entirely different from the cases of aqueous solutions. Accordingly, the mechanism of the micelle formation in the benzene solution seems to be quite different from that in the aqueous solution.

The author wishes to express his thanks to Prof. H. Akamatsu for his suggestions.

Summary

Fatty acid salts of higher aliphatic amines were prepared and used as detergents. The micelle formation in the benzene solution was verified from the relation between the van't Hoff factor and the concentration. It was shown that the amount of solubilized

water is proportional to the concentration of the detergent. The value of the critical micelle concentration was determined from the extraporation of the proportionality. This value is within the region of the remarkable decrease in the curve between the van't Hoff factor and the concentration. With the increases of the carbon number of the amine or the acid part, the critical micelle concentration increases and the solubilizing power decreases. This result is quite different from that of aqueous solutions.

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