Studies on Micelle Formation in Non-polar Solvent by Thermistor

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(Received November 30, 1957)

It will be useful for the study of micelle formation to know the aggregation number at varying temperature. The measurement of vapor pressure depression is one of the several methods applicable to this purpose. The accuracy of the measurement has been recently increased, and the operation has become handy by the use of the thermistor which was also used for the study on micelle formation in the aqueous solution[1].

In order to obtain the aggregation number and the critical micelle concentration and to calculate the change in the thermodynamic value for micelle formation of detergents in the non-polar solvent, measurements on the vapor pressure depression and its temperature dependence were carried out using a pair of thermistors.

Experimental

Materials: Dodecylammonium benzoate, dodecylammonium butyrate and dodecylammonium caprylate were used as detergents, the preparation of which was reported already[2,3]. Cyclohexane for spectrophotometric use was employed as the solvent.

Apparatus: The vapor pressure depression was measured by making use of a couple of matched thermistors. The principle of the measurement was similar to those of McBain et al.[1], Müller et al.[4] and Davies et al.[5] Two thermistors used had resistances of 5040 and 4790 Ω at 19.9°C and the equal mean temperature coefficient of 3.7% per degree between 20° and 30°C. A Wheatstone bridge was employed for measuring the resistance change of the thermistors. Two adjacent arms were occupied by both thermistors. A fixed arm was a standard resistor of 1,000 Ω. The balancing arm consisted of a five dial resistor (R_x), variable in 0.1 Ω step. A galvanometer was a lamp-scale type having a sensitivity of 8.22×10^{-10} A per mm. The voltage which was applied potentiometrically was maintained at 0.4 V throughout the whole experiment. The cell containing both thermistors was similar to that of McBain et al.[1] and was kept in a thermostat controlled to ±0.0005°C. The well of the solvent which developed the atomosphere of the saturated vapor had been placed on the bottom of the cell.

Method: First, solvent drops were placed on both thermistors and R_x(solvent$\sim$solvent) was measured, the bridge being balanced. Next, a solvent and a solution drop were placed on each thermistor and R_x(solvent$\sim$solution) balance was also obtained. The relation between mole fraction of a solute (N) and $\varDelta R_x = R_x(\text{solvent}\sim\text{solvent}) - R_x(\text{solvent}\sim\text{solution})$ was obtained with the cyclohexane solution of naphthalene, ranging from 0.0005 to 0.002 of N. This concentration range was chosen, because it will be safely assumed that the solutions are ideal. The result was as follows: $N=k\cdot\varDelta R_x$. The values of the proportional constant k were 2.04×10^{-3} and 2.12×10^{-3} ohm^{-1} at 19.7° and 31.1°C, respectively. The measurement carried out with the cyclohexane solutions of diphenyl gave consistent values of k. $\varDelta R_x$ was then measured for the detergent solutions with a method similar to that mentioned above at 19.7° and 31.1°C. The apparent mean aggregation number (Z) was calculated by the following equation 1:

$$Z=\frac{m}{k\cdot\varDelta R_x}\,\frac{M_s}{1000} \tag{1}$$

where m and M_s are the molality of the detergent and the molecular weight of the solvent, respectively; $Z=M/M_0$(M and M_0 are the apparent mean micellar weight measured and the monomeric molecular weight of the detergent, respectively). Hence, Z has been evaluated by involving both monomer and micelle. The measurement of R_x(solvent$\sim$solvent) was always carried out before and after that of R_x(solvent$\sim$solution) throughout the whole measurement in order to ensure constancy in the thermistor conditions. $\varDelta R_x$ was measured several times and the average value was adopted for the calculation of Z.

Results and Discussion

Monomer Concentration and Aggregation Number.—The values of Z calculated at 20° and 31°C are given in Table I. The fluctuation in the values of Z was not beyond ten per cent.

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[1] A. P. Brady, H. Huff and J. W. McBain, *J. Phys. and Colloid Chem.*, **55**, 304 (1951).

[2] A. Kitahara, This Bulletin, **30**, 586 (1957).

[3] A. Kitahara, ibid., **28**, 234 (1955).

[4] R. H. Müller and H. J. Stolten, *Anal. Chem.*, **25**, 1103 (1953).

[5] M. Davies and D. K. Thomas, *J. Phys. Chem.*, **60**, 763, 767 (1956).

TABLE I

THE VALUES OF Z, λ AND C_1

Detergent	Concentration			Z		Kreuzer's Treatment				Least Square Method			
	C (millimole/l)		$N\times10^4$ (mole fraction)			C_1 (millimole/l)		λ		C_1 (millimole/l)		λ	
	20°	31°		20°	31°	20°	31°	20°	31°	20°	31°	20°	31°
Dodecyl-ammonium benzoate	22	22	26	3.6	2.9	4.7	5.4	—	10	2	$2._3$	12	6
	27	27	32	4.8	3.8	4.8	5.2						
	34	—	40	7.0	—	4.6	—						
	37	36	42	7.4	4.2	4.5	5.4						
	44	43	51	8.3	4.4	4.6	5.6						
	55	54	63	9.1	5.3	4.7	6.2						
Dodecyl-ammonium caprylate	22	22	$25._4$	1.8	1.6	8.8	9.5	7±1	4	10	6	6.5	2.6
	33	32	38	2.1	2.1	9.8	$10._2$						
	45	44	$52._5$	3.2	2.3	9.3	$11._3$						
	66	64	76	3.6	2.2	9.8	$14._0$						
Dodecyl-ammonium butyrate	23	23	26	2.3	1.5_5	6.7	$10._6$	9±1	6±1	8	10	8.5	6
	34	33	$39._5$	3.1	2.2_5	6.7	$10._8$						
	45	44	48	3.5	2.6_5	7.2	$11._3$						
	68	66	79	4.4	3.5_5	7.2	$11._9$						

TABLE II

CRITICAL MICELLE CONCENTRATION (millimole/l)

	Kreuzer's treatment		Solubilization mothod		Spectral method	
	20°	30°	20°	30°	20°	30°
Dodecylammonium benzoate	4.6	5.2	12±2	15±2	12±1	12±1
Dodecylammonium caprylate	8.3±0.2	9.1±0.1	16±2	16±2	—	—
Dodecylammonium butyrate	6.3±0.2	10	2±1	2±1	—	—

According to Kreuzer5,6), the general equation 2 is obtained without making any assumption as to the nature of the associative equilibria involved.

$$\ln(1/\alpha)=(Z-1)/Z+\int_0^N\{(Z-1)/ZN\}\mathrm{d}N \quad (2)$$

where α is the fraction of the monomer and N the total concentration of the solute in terms of mole fraction as monomer. The monomer concentration (C_1) at each concentration are obtained from the values of α which are graphically calculated from the above equation. These values of C_1 are tabulated in Table I. They are nearly independent of the concentration of detergents.

It has scarcely ever been subjected to experimental studies whether micelles should be monodisperse or not in the non-polar solvent. It was shown in ultraviolet absorption spectra of cyclohexane solutions of dodecylammonium benzoate that the extinction coefficient of the solute molecule participating in micelle formation is almost constant within a concentration range above the critical micelle concentration (*cmc*)2). This fact seems to be an evidence that the micelle is approximately monodisperse within this range. If the aggregation of the monomer to only one species of λ-mer is assumed*, the special relation 3 is deduced :6,7)

$$Z=\lambda-(\lambda-1)\alpha\cdot Z \qquad (3)$$

where λ is the true aggregation number evaluated by subtracting the coexisting monomer. The values of λ are graphically obtained from the plot of Z vs. $\alpha\cdot Z$. They are also shown in Table I. The λ value for dodecylammonium benzoate at 20°C was not successfully obtained because of the scattering of the plots.

The equation 3 is transformed into the following equation, using the molar concentration :

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6) J. Kreuzer, *Z. physik. Chem.*, **B53**, 213 (1942).

* If a whole sequence of aggregates occurs with successive stages and the equilibrium constant at each stage is all equal, the equilibrium constant K must be described as $N(Z\text{-}1)/Z$. The values of K calculated for each concentration using this formula were not constant. Hence, such process of aggregation was not taken into consideration.

7) I. Prigogine and R. Defay, "Chemical Thermodynamics" p. 422, Longmans Green and Co., London, 1954.

$$C - \lambda C/Z + (\lambda-1)C_1 = 0$$

where C is the analytical concentration of the detergent. The values of λ and C_1 were calculated by the least square method with this equation, assuming that λ and C_1 are constant. The resulting values are given in Table I. The first value of Z was not adopted for the calculation in the case of dodecylammonium benzoate at 20°C. It is seen in Table I that these values of C_1 and λ are properly consistent with those of C_1 and λ which were calculated from the equations 2 and 3. The values of λ are comparable with those of Singleterry et al. in benzene solutions of dinonylnaphthalene sulfonate[8].

The *cmc* is obtained by plotting C_1 obtained from the equation 2 vs. C and by extrapolating to $C_1=C$. They are given in Table II and the *cmc* obtained by other methods are also shown in the table for the comparison. The agreement among these values seems to be satisfactory, when it is considered that they have been obtained by independent methods.

TABLE III

THE VALUES OF SOLUBILIZING POWER

	20°	30°
Dodecylammonium benzoate	4.7	4.0
Dodecylammonium caprylate	3.2	2.5
Dodecylammonium butyrate	20	15

It is seen from Table I that the values of λ decrease with the increase in the temperature. This corresponds qualitatively to the change of the solubilizing power with the temperature which is shown in Table III. No quantitative proportionality between them is found. The solubilizing power is defined as the moles of water solubilized per one mole of a detergent.

Calculation of Changes of Thermodynamic Values.—The *cmc* obtained from the Kreuzer's equation may be safely used for the quantitative treatment, though the C_1 obtained by the least square method is not quantitative. When the micelle is considered as the condensed phase, the following equation is deduced:[9]

$$\frac{d\ln(cmc)}{dT} = -\frac{\Delta H}{RT^2} \qquad (4)$$

where ΔH is the change of heat content associated with micelle formation at the mean temperature (25°C). ΔH was calculated from the equation 4 by the use of the *cmc* in the 2nd and 3rd columns in Table II. ΔH is independently obtained from the temperature dependence of the equilibrium constant for the λ-mer aggregation of the monomer. Thus ΔH was again calculated by the use of the λ and C_1 obtained by the least square method. These vlaues for ΔH and related ΔS are given in Table IV.

TABLE IV

THE VALUES OF ΔH AND ΔS ASSOCIATED WITH MICELLE FORMATION

	ΔH(kcal/mole)		ΔS(cal/deg/mole)	
	from *cmc*	from λ and C_1	from *cmc*	from λ and C_1
Dodecyl-ammonium benzoate	−1.9	−5.9	−6.4	−20
Dodecyl-ammonium caprylate	−1.7±0.5	−5.3	−5.7±1.7	−18
Dodecyl-ammonium butyrate	−7.5±0.5	−7.5	−25±1.7	−25

The values obtained from these separate methods agree roughly with each other; hence they may be accepted as the probable values for micelle formation in the non-polar solvent. The absolute values of the heat change for micelle formation in the non-polar solvent seem to be somewhat greater than those in the aqueous solutions[9,10]. This may be due to the dipolar force or the hydrogen bonding which will participate in micelle formation of these detergents.

Summary

The apparent mean aggregation number (Z) of dodecylammonium carboxylate in cyclohexane was obtained from the vapor pressure depression measurement by the use of a pair of thermistors. The monomer concentration (C_1) was calculated from Kreuzer's equations. The C_1 was nearly independent of the concentration. The true aggregation number (λ) was obtained, assuming that the micelle is monodisperse. The *cmc* extraploated from C_1 agreed approximately with those by other methods.

The change of the heat content associated with micelle formation was calculated from the change of the *cmc* with

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[8] S. Kaufman and C. R. Singleterry, *J. Colloid Sci.*, **10**, 139 (1955).

[9] G. Stainby and A. E. Alexander, *Trans. Faraday Soc.*, **46**, 587 (1950).

[10] E. Hutchinson and L. Winslow, *J. Phys. Chem.*, **58**, 1125 (1954). E. D. Goddard and G. C. Benson, *Trans. Faraday Soc.*, **52**, 409 (1956).

the temperature and from the temperature dependence of the equilibrium constant for the λ-mer aggregation. Both agreed roughly with each other.

The author acknowledges the advice on the use of the thermistor given by Mr. Hisao Futaki in the Central Research Institute of Hitachi Manufacturing Co., and thanks Professor Hideo Akamatu for his continuing interest in this study.

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