Studies of Aggregation of Dodecylammonium Carboxylates in Carbon Tetrachloride by Infrared Absorption Spectra and Thermistors

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It was reported that the phenomenon of solubilization by some detergents takes place in carbon tetrachloride solutions as happens in other non-polar solvents[1], though Palit et al.[2] had reported the occurrence of erratic behavior in carbon tetrachloride. Hence, it is considered necessary to investigate micelle formation or aggregation in carbon tetrachloride solutions of detergents by some direct method.

For the present purpose, studies by infrared spectroscopy and on the vapor pressure depression by the use of a couple of thermistors were carried out at varying concentrations. Results obtained by both of these independent methods were compared.

Experimental

Materials. — Dodecylammonium butyrate and dodecylammonium caprylate, the preparation of which had been described previously[1], were employed as detergents. Carbon tetrachloride was distilled after drying over calcium chloride or phosphorus pentoxide and the constant boiling center cut used.

Measurements. — Infrared spectra were obtained using a Perkin-Elmer 21 instrument with rock salt optics. Cells of 1 and 0.5 mm. thickness were used. Room temperature was controlled to about 20°C. Measurements of vapor pressure depressions using a couple of matched thermistors made it possible to calculate the apparent mean aggregation number (Z) which is evaluated involving the monomer present. The apparatus and the method were the same as those described in the previous paper[3]. The temperature of thermostat was controlled to 19.7 ± 0.0005°C. The calibration curve of the thermistor resistance vs. concentration was made using carbon tetrabromide as solute, because it will be safely said that solutions of carbon tetrabromide in carbon tetrachloride are ideal. Measurements by thermistors were made in triplicate or quadruplicate at each concentration and the average value was adopted for the calculation of Z.

Results and Discussion

Assignment of Infrared Spectra.—The infrared spectra of detergents in carbon tetrachloride were depicted in Fig. 1 ranging from 1600 to 1750 cm^{-1} at varying concentrations. Absorption bands which become remarkable with increasing concentration are found at 1640 cm^{-1} in both spectra of dodecylammonium butyrate and

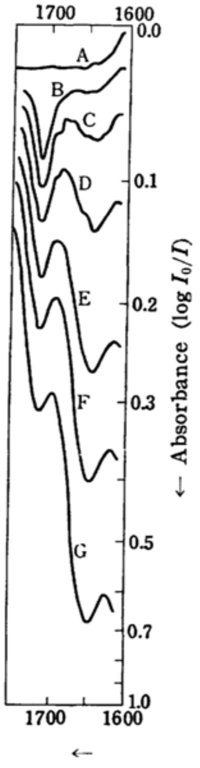

Fig. 1 (a). Change in infrared spectra of dodecylammonium butyrate with varying concentration. (A) pure solvent; (B) 0.0025mole/l.; (C) 0.0050 mole/l.; (D) 0.010 mole/l.; (E) 0.020 mole/l.; (F) 0.030 mole/l.; (G) 0.050 mole/l. Cell length: 1 mm.

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[1] A. Kitahara, *J. Colloid Sci.*, **12**, 342 (1957).
[2] S. R. Palit and V. Venkateswarlu, *Proc. Roy. Soc.*, **A208**, 542 (1951).
[3] A. Kitahara, This Bulletin, **31**, 288 (1958).

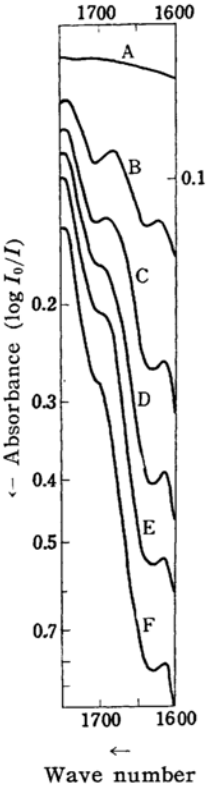
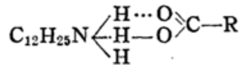
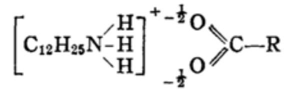


Fig. 1 (b). Change in infrared spectra of dodecylammonium caprylate with varying concentration. (A) pure solvent; (B) 0.018 mole/l.; (C) 0.036 mole/l.; (D) 0.055 mole/l.; (E) 0.073 mole/l.; (F) 0.112 mole/l. Cell length: 0.5 mm.

caprylate. On the other hand, it is seen that the absorption bands of 1710 cm^{-1} in neither of these spectra are sensitively variable with increasing concentration. Yeager and Barrow[4] have shown from infrared spectra of the reaction products of acetic acid and *n*-butylamine, diethylamine or triethylamine that the absorption bands of 1712 and 1630 cm^{-1} are assigned to the carbonyl group forming a hydrogen bonds with the same or another molecule and to the NH_2^+ or NH_3^+ group of the ammonium salt, respectively. The absorption band of "Amino-Acid I" which falls within the narrow range of 1640~1610 cm^{-1} for many monoamino-monocarboxylic acids has been assigned to NH_3^+ by many authors[5]. Hence, it may be concluded that the absorption bands of 1710 and 1640 cm^{-1} belong to the molecules of following formulae A and A$_1$, respectively:


(A)


(A$_1$)

It will be thought that the molecule of A$_1$ aggregates to λ-mer in a non-polar solvent by virtue of ionic parts. Then the following equilibrium will exist in the carbon tetrachloride solutions:

$$A \rightleftarrows A_1 \rightleftarrows 1/\lambda A_\lambda \qquad (1)$$

where A_λ represents a λ-mer molecule. It is safely assumed that aggregation does not affect the absorption band, because aggregation will not be so strong as to affect chemical bonding, and that the greater part of molecules of A$_1$ exists in the aggregated state instead of the monomeric form because of the highly polar part. Hence, the equilibrium 1 can be rewritten as follows:

$$\lambda A \rightleftarrows A_\lambda \qquad (2)$$

The absorption bands of 1710 and 1640 cm^{-1} are characteristic for the molecule existing as monomer and the one taking part in aggregation, respectively. This assignment is consistent with the fact that the infrared spectra of these detergents by the potassium chloride disc method which represent the absorption band in the solid state show the more intense absorption at the 1640 cm^{-1} than those of the relatively concentrated solutions and show no absorption at the 1710 cm^{-1}. The absorbances ($\log I_0/I$) of each absorption band, which are shown in Table I, were obtained using the base-line method and the peak-intensity method from Fig. 1.

Analysis of Absorbance Data.—Aggregation equilibrium of a detergent in a non-polar solvent can be described by the Equation 2. The true aggregation number λ is evaluated by excluding the monomer present in the solution. It may be assumed that the aggregates are approximately monodisperse in a non-polar solution of the detergents[3]. No shift in the absorption band of 1640 cm^{-1} which is characteristic for the aggregate is evident from Fig. 1. This fact may be considered as an evidence of forming a single kind of aggregation[6]. The equilibrium constant is represented using molar concentration instead of activity, which is valid

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[4] E. A. Yeager and G. M. Barrow, *J. Am. Chem. Soc.*, **76**, 5211 (1954); **77**, 4474, 6206 (1955).

[5] L. T. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen and Co., London, (1954), p. 204.

[6] N. D. Coggeshall and E. L. Saier, *J. Am. Chem. Soc.*, **73**, 5414 (1951).

TABLE I

THE VALUES OF ABSORBANCE (cell thickness: 1 mm.)

Dodecylammonium Butyrate					Dodecylammonium Caprylate				
Concentration (mole/l.)	Absorbance				Concentration (mole/l.)	Absorbance			
	D_a		D_1			D_a		D_1	
	B. L.*	P. I.*	B. L.	P. I.		B. L.	P. I.	B. L.	P. I.
0.0025	0.010	0.018	0.047	0.060	0.018	0.034	0.20_8	0.050	0.13_7
0.0050	0.016	0.050	0.053	0.082	0.036	0.080	0.47_2	0.050	0.23
0.010	0.035	0.11_5	0.055	0.11	0.055	0.18	0.76_4	0.060	0.29
0.020	0.070	0.24_5	0.065	0.15_5	0.073	0.24	1.02	0.060	0.36_4
0.030	0.12	0.38	0.075	0.21	0.112	0.42	1.62	0.070	0.50_4
0.050	0.23	0.65_7	0.085	0.28_5					

* B. L. ...Base line method, P. I. ...Peak intensity method

for the dilute concentration range under consideration. That is,

$$C_\lambda/C_1{}^\lambda=K \qquad (3)$$

where C_λ and C_1 are the molar concentration of λ-mer and monomer, respectively. Beer's law of absorption is approximately obeyed for absorption bands of the monomer and of the detergent molecule taking part in aggregation in these dilute concentration ranges. Hence,

$$\left.\begin{aligned}(\log I_0/I)_1&=k_1C_1l=D_1\\(\log I_0/I)_a&=k_aC_al=D_a\end{aligned}\right\} \qquad (4)$$

where k, C and l are the extinction coefficient, the molar concentration in monomer unit and a length of the cell, respectively. The subscripts of 1 and a represent a coexisting monomer and a detergent molecule taking part in aggregation, respectively. By definition,

$$C_a=\lambda C_\lambda \qquad (5)$$

The following equation is deduced from the Equations 3, 4 and 5:

$$\lambda\log D_1-\log D_a+k'=0 \qquad (6)$$

where $k'=\log\{\lambda k_a l K/(k_1 l)^\lambda\}$

As it has been assumed that λ is constant, k' is constant. The values of λ and k' can be calculated by means of the Equation 6 using the data of Table I. The values of λ calculated by means of the least square are given in the 2nd and 3rd columns of Table II.

TABLE II

THE VALUES OF TRUE AGGREGATION NUMBER (λ)

	Spectral method		Thermistor method
	Base line	Peak intensity	
Dodecylammonium butyrate	2.7	2.4	2.8
Dodecylammonium caprylate	3.3	2	3.0

In order to ascertain the result obtained above, the absolute intensity method was employed for comparison. Integrated densities (D_A) of absorption bands were calculated from the values of measurements for both bands of 1640 and 1710 cm^{-1} at a few concentrations of these detergents in carbon tetrachloride. These measurements* were carried out by means of a Perkin-Elmer 112 instrument with calcium fluoride prism. Room temperature was 25±1°C. Integrated density is represented by the following form[7]:

$$D_A=K\ln(I_0/I)_{\nu_{\max}}\Delta\nu_{1/2}$$

where $\ln(I_0/I)_{\nu_{\max}}$ is the apparent peak intensity, $\Delta\nu_{1/2}$ the apparent half-intensity band width and K the constant which is determined by $\ln(I_0/I)_{\nu_{\max}}$ and $S/\Delta\nu_{1/2}$ (S is the slit width). The λ's were calculated from the Equation 6 using the values of D_A instead of the absorbances in Table I. The λ's obtained thus were approximately equal to 2 for both detergents. The agreement between those values and those from the peak intensity in Table II is satisfactory. The difference between the values from the absolute intensity and those from the base line is not serious, since it is sufficient only if we confirm the agreement of the order of magnitude of aggregation.

Analysis of Data by Thermistor.—The apparent mean aggregation numbers Z obtained by the thermistor method are shown in Table III. The fraction of the solute

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* These measurements were carried out in cooperation with Mr. Suetaka by suggestion of Professor K. Kojima of Tokyo Institute of Technology, to whom the author wishes to express his sincere gratitude.

[7] D. A. Ramsey, ibid., **74**, 72 (1952); J. Wenograd and R. T. Spurr, ibid., **79**, 5844 (1957).

TABLE III
THE VALUES OF Z, α, C_1 AND λ

	Concentration (C) (mole/l.)	Z	α	C_1 (mole/l.)	λ
Dodecylammonium butyrate	0.085_5	1.8	0.32	0.026	2.8
	0.050	1.5_5	0.43_5	0.022	2.6
	0.035	1.6	0.47_5	0.016_5	3.6
	0.017	1.2	0.71	0.012	2.1
	0.009	≈ 1.0	≈ 1.0	—	—
Dodecylammonium caprylate	0.111	2.0	0.24	0.027	3.0
	0.073	1.7_5	0.31	0.023	2.7
	0.055	1.7_5	0.35_5	0.020	3.0
	0.036_5	1.6_5	0.43	0.016	3.2
	0.018	≈ 1.0	≈ 1.0	—	—

present as the monomer (α) which is equal to C_1/C can be calculated by means of the following Kreuzer's equation[8]:

$$\ln(1/\alpha)=(Z-1)/Z+\int_0^C \{(Z-1)/ZC\}\mathrm{d}C \quad (7)$$

where C is the total concentration of the solute. The values of C_1 are, therefore, calculated at each total concentration. The values of α and C_1 are given in the 4th and 5th columns of Table III. The following relations are deduced for the equilibrium 2 under an assumption that λ and K are constant[8,9]:

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

$$\text{or} \qquad \lambda=(1-\alpha)/(1/Z-\alpha). \qquad (8)$$

The values of the true aggregation number λ calculated using the Equation 8 are given in the last colum of Table III. The mean values of λ are given in the 4th column of Table II.

It is evident from Table II that the agreement between the values of λ obtained by both spectral and thermistor methods is satisfactory as for the order of magnitude of aggregation. This gives us an evidence to an assumption made in the derivation of the Equation 8. The true aggregation numbers λ of these detergents in carbon tetrachloride solutions are relatively smaller than those in cyclohexane solutions[3]. This fact corresponds qualitatively to the solubilizing power in carbon tetrachloride which is smaller than that in cyclohexane[1].

The Critical Micelle Concentration.— These aggregates may be regarded as small micelles. It has been shown experimentally[10] and theoretically[11] that formation of small micelles gradually takes place over an extended range of concentration. Hence, the critical micelle concentration (cmc) may not be sharply determined. The values of the cmc were tentatively evaluated by plotting C_1 in Table III vs. C and extrapolating to $C_1=C$. These cmc's are 0.010±0.001 and 0.013±0.001 mole/l. for dodecylammonium butyrate and caprylate, respectively. The plot of absorbance (D_1 and D_a) from base line method vs. total concentration (C) was depicted in Fig. 2.

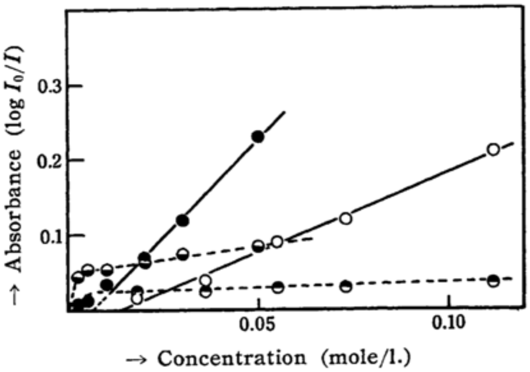

Fig. 2. Plots of absorbance (log I_0/I) versus concentration.

○ Plot for absorption at 1640 cm^{-1} of dodecylammonium caprylate
◓ Plot for absorption at 1710 cm^{-1} of dodecylammonium caprylate
Cell length, 0.5 mm.

● Plot for absorption at 1640 cm^{-1} of dodecylammonium butyrate
◒ Plot for absorption at 1710 cm^{-1} of dodecylammonium butyrate
Cell length, 1 mm.

It is evident from Fig. 2 that the relation between D_a and C is approximately linear excepting the range of lower concentra-

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[8] J. Kreuzer, *Z. physik. Chem.*, **B53**, 213 (1943).

[9] I. Prigogine and R. Defay, "Chemical Thermodynamics", Longmans Green and Co., London, (1954), p. 422.

[10] E. F. Williams, N. T. Woodberry and J. K. Dixon, *J. Colloid Sci.*, **12**, 452 (1957).

[11] J. Stauff, *Z. Elektrochemie*, **59**, 246 (1995).

tions in the case of dodecylammonium butyrate where the experimental error is appreciable. It will be reasonable to assume that extrapolation of the $D_a \sim C$ line to zero concentration shows the cmc. These cmc's are 0.007±0.001 and 0.013±0.002 mole/l. for dodecylammonium butyrate and caprylate, respectively. The values obtained using the peak intensity by a similar way were 0.002±0.001 and 0.006±0.002mole/l., respectively. The agreement between the cmc's obtained by spectral and thermistor method is satisfactory as for the order of magnitude. On the other hand, these cmc's do not show good concordance with values obtained by solubilization of water which were 0.016±0.002 and 0.035±0.005 mole/l.*, respectively. This may be considered to indicate that the cmc has an extended range of concentration or that the cmc may be affected by the presence of water.

Solubilization which takes place in these solutions may be a type similar to that by adsorption on polar groups of small micelles by McBain et al.[12], though polar groups will be properly present in the interior of the aggregate in these non-polar solutions.

Summary

Measurements of infrared absorption spectra and of vapor pressure depressions using a couple of matched thermistors were carried out with carbon tetrachloride so tions of dodecylammonium carboxyla at varying concentrations. The absor tion bands at 1710 and 1640 cm^{-1} we assigned to the carbonyl group of the monomer molecule which is formed by hydrogen bonding between amine and acid, and to the NH_3^+ group of ammonium salt resulting from the aggregation, respectively. The equation which was derived from the Beer's law and the aggregation equilibrium made it possible to calculate the true aggregation number λ using the values of absorbance at each absorption band.

Alternatively, the λ was calculated by means of the Kreuzer's equation from the apparent mean aggregation number Z which was obtained using thermistors. The agreement between the λ's obtained by the spectral and thermistor methods was satisfactory as for the order of magnitude. The cmc was tentatively estimated by both spectral and thermistor method. The agreement between the cmc's obtained by these independent methods was good. But these cmc's did not show good agreement with those obtained from solubilization.

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* These values are those at 18±2°C instead of those at 26°C in Ref. 1.

[12] J. W. McBain and H. McHan, *J. Am. Chem. Soc.*, **70**, 3838 (1948).