

THE EFFECT OF PRESSURE ON MICELLE FORMATION AND SOLUBILITY OF HEXADECYLTRIMETHYLAMMONIUM BROMIDE IN WATER

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The conductivities of hexadecyltrimethylammonium bromide (HTAB) in water have been measured in the concentration range $2 \times 10^{-4} \sim 4 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ at pressures up to 2500 kg/cm^2 at 25°C , and used to determine the critical micelle concentrations (c.m.c.) and the apparent solubilities. The limiting equivalent conductivities of hexadecyltrimethylammonium ion, λ° (HTA^+) decrease with increasing pressure. The c.m.c. increase with the increase in pressure up to about 1000 kg/cm^2 and decrease at higher pressures. The fact that the maximum pressure of the c.m.c. of HTAB is not so much different from those of the lower homologues appears to indicate that there occurs no solidification at the maximum pressure. The partial molal volume change accompanying the micelle formation at 1 atm, $\Delta \bar{V}^\circ$ is $10 \text{ cm}^3 \cdot \text{mol}^{-1}$, being calculated from the pressure dependence of the c.m.c. The rate of decrease in the apparent solubilities of HTAB with increasing pressure is very large up to about 1500 kg/cm^2 and rather small at higher pressures.

Introduction

The hydrophobic hydration of alkylammonium ions with the carbon number in the alkyl chain less than 8 has been investigated conductimetrically at high pressures by the present authors^{1,2)}. In the present paper, the work has been extended to a hexadecyltrimethylammonium ion (HTA^+) having a longer alkyl chain, for the hydration of this alkylammonium ion is influenced more effectively by hydrophobic hydration than by coulombic hydration.

The alkylammonium salt having a long alkyl chain forms micelles at a suitable concentration, temperature and pressure. While the surfactants whose critical micelle concentrations (c.m.c.) have been studied at high pressure^{3~7)} have 8~12 carbon atoms in the longest alkyl chain, the hexadecyltrimethylammonium bromide (HTAB) studied here has 16 carbon atoms in the main alkyl chain. The c.m.c. of the surfactants so far investigated has a maximum against pressure at about 1000 kg/cm^2 . One of the factors explaining the decrease in the c.m.c. at high pressures may be partial solidification

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* $1 \text{ kg/cm}^2 = 0.9807 \times 10^5 \text{ Pa}$

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2) M. Ueno, *ibid.*, **45**, 61 (1975)

3) S. D. Hamann, *J. Phys. Chem.*, **66**, 1359 (1962)

4) R. F. Tuddenham and A. E. Alexander, *ibid.*, **66**, 1839 (1962)

5) J. Osugi, M. Sato and N. Ifuku, *This Journal*, **35**, 32 (1965)

6) M. Tanaka, S. Kaneshina, T. Tomida, K. Nōda and K. Aoki, *J. Colloid Interface Sci.*, **44**, 525 (1973)

7) M. Tanaka, S. Kaneshina, K. Shin-no, T. Okajima and T. Tomida, *ibid.*, **46**, 132 (1974)

in the interior of the micelles³⁾. If it is the case, the pressure at which the micelles might be solidified would perhaps depend on the carbon number in the alkyl chain of the surfactants. Thus it is interesting to investigate how the maximum pressure of the c. m. c. will vary with the carbon number in the alkyl chain.

The temperature effect on the solubility of the surfactants is very peculiar compared with the simple salts, as can be seen from the fact that the solubility curve of the surfactants has a Kraft point. Pressure also gives a corresponding influence on the solubility of the surfactants in water^{5,6,8)}. To make sure of such a phenomenon, the apparent solubilities of HTAB have been measured as a function of pressure by the electric conductivity method.

Experiment

Material

HTAB of guaranteed reagent grade was obtained from Nakarai Chem. Co., Ltd. It was recrystallized three times from ethanol-acetone solutions. The critical solubility temperature of HTAB is $21\sim 24^{\circ}\text{C}$ ⁹⁾. Distilled water was passed through an ion exchange column prior to use. The small conductivity of the conductivity water was subtracted from the total electrolytic conductivity of the solution at each pressure. The specific volume, the dielectric constant and the viscosity of water at high pressures were taken from Refs. (10), (11) and (12), respectively. These physical properties were assumed to be equal to those of dilute aqueous solutions of HTAB at high pressures.

Apparatus

The high pressure conductivity cell was made of glass and has a teflon piston with an O-ring as shown in Fig. 1. The platinum electrodes were lightly platinized to minimize the effects of polarization.

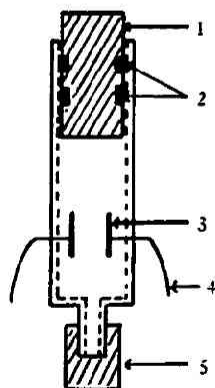


Fig. 1 Conductivity Cell

- 1: Teflon piston 2: O-ring
3: Platinum electrodes 4: Electrical leads
5: Teflon cap

- 8) S. D. Hamann, *This Journal*, **35**, 109 (1965)
9) N. K. Adam and K. G. A. Pankhurst, *Trans. Faraday Soc.*, **42**, 523 (1946)
10) G. S. Kell and E. Whalley, *Phil. Trans. Roy. Soc. London*, **258A**, 565 (1965)
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12) J. B. Cappi, Ph. D. Thesis, London University (1964)

The cell constant at atmospheric pressure was determined by using 2×10^{-3} N KCl solution¹³⁾ and it was assumed that the cell constant did not vary at high pressures. The high pressure apparatus and the method of conductivity measurements were described elsewhere¹⁴⁾. Pressure was measured with an accuracy of ± 10 kg/cm² by a Bourdon gauge calibrated to the free piston gauge of Kobe Steel Co., Ltd. The temperature of the thermostat in which the pressure vessel was immersed was controlled within $\pm 0.02^\circ\text{C}$.

Results and Consideration

Limiting equivalent conductivity

The conductivity data are given in Table 1. The limiting equivalent conductivities of HTAB, $\Lambda^\infty(p)$ (HTAB) were obtained by the least square method using the conductivities, Λ below the c. m. c. The slope of the $\Lambda - \sqrt{C}$ plots obtained at each pressure is about 15% larger than the theoretical Onsager slope for the 1 : 1 electrolyte. Scott and Tartar¹⁵⁾ reported that HTAB confirmed the Onsager theory within the limits of experimental errors. However, Bair and Kraus¹⁶⁾ communicated that for the hexadecyl and octadecyl salts the slopes were approximately 75% greater than that predicted for a 1 : 1

Table 1 Electrolytic conductivities κ (ohm⁻¹·cm⁻¹) and equivalent conductivities Λ (ohm⁻¹·cm²·equiv⁻¹) of hexadecyltrimethylammonium bromide in water at 25°C

$C \times 10^4$ (molarity) at 1 atm	1 atm		400 (kg/cm ²)		800 (kg/cm ²)		1200 (kg/cm ²)	
	$\kappa \times 10^5$	Λ	$\kappa \times 10^5$	Λ	$\kappa \times 10^5$	Λ	$\kappa \times 10^5$	Λ
2.474	2.407	97.3	2.467	98.0	2.509	97.9	2.523	97.3
4.003	3.876	96.8	3.974	97.6	4.035	97.6	4.066	97.0
6.000	5.790	96.5	5.935	97.3	6.023	97.2	6.069	96.6
6.603	6.367	96.4	6.537	97.3	6.633	97.3	6.668	96.4
8.007	7.689	96.0	7.884	96.8	8.005	96.8	8.067	96.2
8.037	7.716	96.0	7.913	96.8	8.038	96.8	8.096	96.2
9.014	8.644	95.9	8.867	96.7	9.004	96.7	9.065	96.0
11.00	9.413	85.5	9.995	89.3	10.23	90.0	10.19	88.4
12.01	9.633	80.2	10.23	83.7	10.47	84.4	10.44	83.0
12.06	9.652	80.0	10.24	83.5	10.48	84.2	10.44	82.7
16.07	10.61	66.0	11.24	68.8	11.49	69.2	11.45	68.0
21.96	11.98	54.6	12.61	56.4	12.87	56.8	12.83	55.8
39.95	16.21	40.6	16.90	41.6	17.19	41.7	17.19	41.1
40.10	16.20	40.4	16.88	41.4	17.19	41.5	17.16	40.9
C. m. c. $\times 10^4$ (molarity)	9.35 ± 0.04		9.99 ± 0.04		10.26 ± 0.04		10.25 ± 0.04	

13) G. C. Benson and A. R. Gordon, *J. Chem. Phys.*, **13**, 473 (1974)

14) M. Ueno, K. Shimizu and J. Osugi, *This Journal*, **43**, 33 (1973)

15) A. B. Scott and H. V. Tartar, *J. Amer. Chem. Soc.*, **65**, 692 (1943)

16) E. J. Bair and C. A. Kraus, *ibid.*, **73**, 1129 (1951)

salt and suggested the dimerization of the long chain ions of 16 or more carbon atoms. It seems very difficult to conclude that 15% deviation from the theoretical slope is attributed to the dimerization of HTA⁺ in view of the experimental error. Hence we assume here in the discussion of the pressure dependence of the c.m.c. and the solubility that HTAB behaves in water as a 1:1 electrolyte below the c.m.c.

The limiting ionic equivalent conductivities at high pressures, $\lambda^{\circ}(\rho)$ were determined as follows. $\Lambda^{\circ}(\rho)(\text{KBr})$ is 151.64 taken from Ref. (13), and the ratios of $\Lambda^{\circ}(\rho)(\text{KBr})$ to $\Lambda^{\circ}(\rho)(\text{KBr})$ were calculated from the data in Ref. (17). Combining $\Lambda^{\circ}(\rho)(\text{KBr})$ with the transference numbers of KBr in water at high pressures¹⁸⁾, $\lambda^{\circ}(\rho)(\text{Br}^-)$ were obtained. $\lambda^{\circ}(\rho)(\text{HTA}^+)$ were determined by subtracting $\lambda^{\circ}(\rho)(\text{Br}^-)$ from $\Lambda^{\circ}(\rho)(\text{HTAB})$, and are given in Table 2 together with the ionic Walden products, $\lambda^{\circ}(\rho)(\text{HTA}^+)$

Table 2 Limiting equivalent conductivities ($\text{ohm}^{-1}\text{cm}^2\text{equiv}^{-1}$) and Walden products $W(\text{ohm}^{-1}\text{cm}^2\text{equiv}^{-1}\text{cP})$ of hexadecyltrimethylammonium ion in water at 25°C

$P(\text{kg/cm}^2)$	Λ°	$\lambda^{\circ}(\text{Br}^-)$	$\lambda^{\circ}(\text{HTA}^+)$	$W(\text{HTA}^+)$
1	98.9 ± 0.1	78.4	20.5	18.3
400	99.6 ± 0.1	79.3	20.3	18.0
800	99.5 ± 0.2	79.6	19.9	17.7
1200	98.8 ± 0.2	79.4	19.4	17.3

is 20.5 being comparable with 20.8 obtained by Bair and Kraus¹⁶⁾. Although $\Lambda^{\circ}(\rho)(\text{HTAB})$ has a maximum against pressure, both $\lambda^{\circ}(\rho)(\text{HTA}^+)$ and the Walden products of HTA⁺ decrease with increasing pressure just as in the cases of other alkylammonium ions^{1,2,19)}. This indicates that the density of water around the HTA⁺ is higher than in the bulk¹⁹⁾.

Critical micelle concentration

The c.m.c. was determined by plotting electrolytic conductivities against the equivalent concentrations of HTAB as shown in Fig. 2, where the point of intersection is taken to be the c.m.c. The values of the c.m.c. determined thus are listed in Table 1. The c.m.c. at 1 atm is $9.35 \times 10^{-4} \text{mol}\cdot\text{dm}^{-3}$, which is larger than $8.2 \times 10^{-4} \text{mol}\cdot\text{dm}^{-3}$ obtained by Barry *et al.*²⁰⁾ and nearer to $9.9 \times 10^{-4} \text{mol}\cdot\text{dm}^{-3}$ by Lawrence and Stenson²¹⁾.

The partial molal volume change involved in the formation of micelles from the free ions, $\Delta \bar{V}$ is determined according to the equilibrium constant derived by Phillips²²⁾ on the basis of the mass action law. Here we consider the equilibrium between the free ions and the micelles as follows:



where M^{Z+} , N and Z represent the micelle, the number of HTA⁺ per micelle and the net charge on the

17) A. B. Gancy and S. B. Brummer, *J. Chem. Eng. Data*, **16**, 385 (1971)

18) J. Osugi, M. Nakahara, Y. Matsubara and K. Shimizu, *This Journal*, **45**, 23 (1975)

19) M. Nakahara and J. Osugi, *ibid.*, **45**, 1 (1975)

20) B. W. Barry, J. C. Morrison and G. F. J. Russel, *J. Colloid Interface Sci.*, **33**, 554 (1970)

21) A. S. C. Lawrence and R. Stenson, *Proc. Intern. Congr. Surface Activity*, 2nd London, 368 (1955)

22) J. N. Phillips, *Trans. Faraday Soc.*, **51**, 561 (1955)

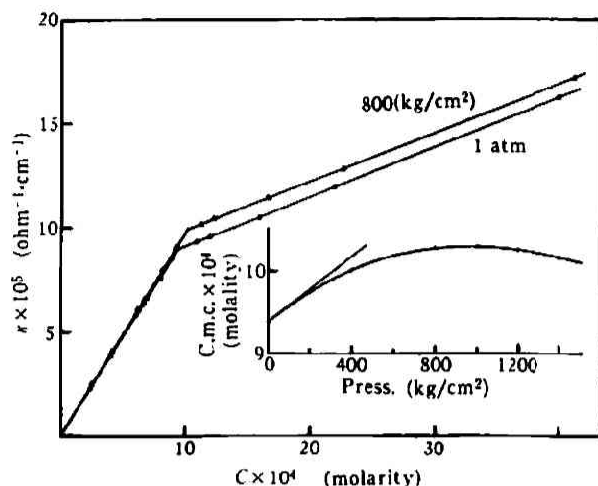


Fig. 2 Plots of electrolytic conductivity, κ , versus concentration of hexadecyltrimethylammonium bromide, C , in water at 25°C, and 1 atm and 800 kg/cm²

Inset: Variation of the c.m.c. with pressure

micelle, respectively. The partial molal volume change accompanying the micelle formation at atmospheric pressure is expressed^{3,4)} by

$$\Delta \bar{V}^{(1)} = RT \frac{\partial}{\partial P} \left\{ \left(2 - \frac{q}{N} - \frac{1}{N} \right) \ln (\text{c.m.c.}) \right\}_T, \quad (2)$$

where q is the effective charge on the micelle and the c.m.c. is expressed in molality. (The molarity is converted into the molality by making the assumption that the density of the dilute solution is equal to that of pure water.) Although the pressure dependences of q and N have not been known yet, we postulate that they are constant at high pressures. Furthermore, $1/N$ in Eq. 2 could be neglected because it is reported that N is about 95²³⁾ and that q/N is 0.091 (in 0.013 mol·dm⁻³ KBr solution)²⁴⁾ and 0.11²⁵⁾. Applying Eq. 2 to the pressure dependence of the c.m.c. and taking $q/N=0.1$, $\Delta \bar{V}^{(1)}$ was determined to be 10 cm³·mol⁻¹. Though $\Delta \bar{V}^{(1)}$ of HTAB in water has not been determined, its value may be estimated by extrapolating the correlation between $\Delta \bar{V}^{(1)}$ and the carbon number in the main alkyl chain of the lower homologues given from the density measurements²⁶⁾; the value determined at present is smaller than the extrapolated one. In this homologous series, $\Delta \bar{V}^{(1)}$ obtained by other workers from the pressure dependence of the c.m.c.^{4,7)} are also smaller than those from the density measurements²⁶⁾.

$\Delta \bar{V}^{(1)}$ of decyltrimethylammonium bromide (DETAB) and dodecyltrimethylammonium bromide (DTAB) recalculated by using Eq. 2 and the data in Refs. (4) and (22) are both 4 cm³·mol⁻¹. The differences in $\Delta \bar{V}^{(1)}$ between HTAB and DETAB and between HTAB and DTAB are equally 6 cm³·mol⁻¹, and the volume increment per methylene group is approximately 1~1.5 cm³·mol⁻¹ which is comparable with 1.3 cm³·mol⁻¹ obtained by Corkill *et al.*²⁶⁾ from the density measurements. The differences between HTAB and the lower homologues might be explained in view of hydrophobic hydration as discussed below. $\Delta \bar{V}^{(1)}$ so far obtained are always positive for both ionic and nonionic surfactants, and increase in magnitude with increase in the carbon number in the main alkyl chain of the surfactant^{26,27)}.

23) P. Ekwall, L. Mandell and P. Solyon, *J. Colloid Interface Sci.*, **35**, 519 (1971)

24) K. J. Mysels, *ibid.*, **10**, 507 (1955)

25) M. J. Vold, *ibid.*, **5**, 506 (1950)

26) J. M. Corkill, J. F. Goodman and T. Walker, *Trans. Faraday Soc.*, **63**, 768 (1967)

27) L. Benjamin, *J. Phys. Chem.*, **70**, 3790 (1966)

Although the reason for the positive $\Delta\bar{V}^{(1)}$ is not definitely known, two important factors to make $\Delta\bar{V}^{(1)}$ positive can be considered. One is due to the electrostriction effect which may be important especially for ionic surfactants. Partial neutralization of the head group by the counterions would bring about a volume increase, being similar to the volume change in the ion-pair formation of inorganic ions³⁾. The other is the effect associated with hydrophobic hydration. The excess molal volumes, $\bar{V}^{\circ E}$ calculated as $\bar{V}^{\circ E} = \bar{V}_2^{\circ} - V_2$, where $\bar{V}_2^{\circ}$ and V_2 are the limiting partial molal volumes of the solutes in water and the molar volumes of the pure solutes in the liquid state, respectively, are generally noticed to be negative for the nonelectrolytes such as alkylamines and alcohols and to increase in magnitude with the increase of the hydrocarbon part of the molecules^{28,29)}. Since the interior of the micelles would be in a liquid state^{27,30)}, the release of water molecules around the alkyl chain on the micelle formation might be considered to make a positive contribution to $\Delta\bar{V}^{(1)}$. If the electrostriction effect makes a large contribution to $\Delta\bar{V}^{(1)}$, it seems difficult to explain that $\Delta\bar{V}^{(1)}$ depends on the carbon number. Thus the differences between HTAB and the lower homologues might be governed mainly by the magnitude of hydrophobic hydration of the free surfactant ions.

As is shown in the inset of Fig. 2, the c.m.c. versus pressure curve has a maximum at about 1000 kg/cm² as in the cases of other surfactants^{3~7)}. If the assumptions in Eq. 2 is valid at high pressure, Eq. 2 gives the negative $\Delta\bar{V}^{(p)}$ above 1000 kg/cm². The partial solidification of the interior of the micelles at high pressure was proposed as one of the factors making $\Delta\bar{V}^{(p)}$ negative³⁾. It is known that the normal hydrocarbons, C₁₆H₃₄, C₁₂H₂₆ and C₁₀H₂₂ freeze at 410, 1650 and 2950 atm at 25°C, respectively³¹⁾. The longer the hydrocarbon, the lower the freezing pressure. But the pressure at which the c.m.c. of HTAB is maximum is not so much different from those of the lower homologues, DTAB and DETAB^{4,7)}. Thus it seems implausible that the interior of the micelles is partially solidified at the maximum pressure. Tanaka *et al.*⁷⁾ showed from the density measurements that the partial molal volumes of alkyltrimethylammonium bromides and sodium alkyl sulfates in the micellar state decrease monotonously with increasing pressure, and suggested that the interior of the micelles remained in the liquid state at least up to 2000 kg/cm².

Apparent solubility

The resistance of the solutions of HTAB suddenly increased at high pressures and did not remain constant. Such a phenomenon was first found by Osugi *et al.*⁵⁾ in aqueous decylammonium chloride solutions, and assured by Hamann⁸⁾ that it is due to the solidification of the solute. The pressure effect on the solubilities of dodecylammonium chloride (DAB) and sodium dodecylsulfate (SDS) in water has been studied so far by Tanaka *et al.*⁶⁾

Fig. 3 shows the relation between the concentration of the solutions and the pressures at which the resistance of the solutions did not remain constant. Since the solution is apt to be superpressed, the solubility curve of Fig. 3 indicates the apparent solubilities of HTAB in water. As is shown in Fig. 3,

28) S. Cabani, G. Conti and L. Lepori, *ibid.*, **78**, 1030 (1974)

29) M. V. Kaulgud and K. J. Patil, *ibid.*, **78**, 714 (1974)

30) K. Shinoda and T. Soda, *ibid.*, **67**, 2072 (1963)

31) P. W. Bridgman, *Proc. Amer. Acad. Arts and Sci.*, **77**, 138 (1948-1949)

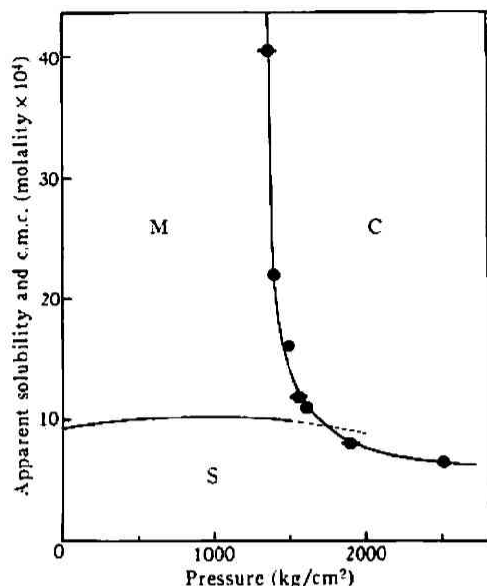


Fig. 3 Variation of the apparent solubility and the c.m.c. of hexadecyltrimethylammonium bromide with pressure; *M* is the area for micellar solution, *S* is the area for singly dispersed solution, and *C* is the area for solid

the solubility curve is expected to have the critical solution pressure⁶⁾ at which the curves of solubility versus pressure and of the c.m.c. versus pressure intersect, corresponding to the Kraft point in the temperature effect on the solubility. The parallelism between temperature and pressure can be also seen in the polymerization of aldehydes and styrenes³²⁾.

For the systems where HTAB in the solid state and the free ions, HTA^+ and Br^- , are in equilibrium, we have

$$\Delta \bar{V}^\circ = \bar{V}^\circ(\text{HTA}^+) + \bar{V}^\circ(\text{Br}^-) - V(\text{HTAB}) = -RT \left(\frac{\partial \ln K_{sp}}{\partial P} \right)_T, \quad (3)$$

where $\Delta \bar{V}^\circ$, $\bar{V}^\circ(\text{HTA}^+)$, $\bar{V}^\circ(\text{Br}^-)$ and $V(\text{HTAB})$ are the partial molal volume change accompanying the dissociation of HTAB in the solid state into the free ions, the limiting partial molal volume of HTA^+ , that of Br^- and the molar volume of HTAB in the solid state, respectively. In Eq. 3, $K_{sp} = m(\text{HTA}^+) \gamma(\text{HTA}^+) \cdot m(\text{Br}^-) \gamma(\text{Br}^-)$, where m and γ are, respectively, the molality and the activity coefficient of the corresponding free ion. Assuming that the variation of the activity coefficients of the free ions with pressure can be neglected, we have

$$\Delta \bar{V}^\circ = -2RT \left(\frac{\partial \ln m}{\partial P} \right)_T. \quad (4)$$

Fig. 3 shows that the apparent solubilities above about 1750 kg/cm² decrease gradually with increasing pressure. If the true solubility curve has the parallelism with the apparent one, $\Delta \bar{V}^\circ > 0$ can be obtained from Eq. 4; the molar volume of HTAB in the solid state is smaller than the sum of the limiting partial molal volumes of the free ions as in the cases of DAB and SDS⁶⁾. Shinoda and Soda³⁰⁾ obtained a similar result for sodium dodecylsulfonate at atmospheric pressure below the Kraft point from the density measurements.

32) K. E. Weale, "Chemical Reactions at High Pressures", Chap. 8 E. & F. N. Spon Ltd. (1967)

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