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MICELLE FORMATION OF CATIONIC DETERGENT SOLUTION
AT HIGH PRESSURES

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The effect of pressure on the critical micellar concentration (c. m. c.) of the aqueous solution of cationic detergents i. e. dodecyl ammonium chloride (DAC), dodecyl trimethylammonium chloride (DTAC) and dodecyl benzyldimethylammonium chloride (DBAC) has been investigated by the conductivity measurement. The c. m. c. of DTAC and DBAC increases with increasing pressure up to about 1000 atm and then it gradually decreases at higher pressures. The DAC solution shows a peculiar behavior. At about 2300 atm its specific conductivity decreases sharply. Assuming the equilibrium between single detergent ions and micelle ions, the partial molal volume change caused by micelle formation is discussed. At 1 atm the ΔV of the above mentioned three substances is about +3 cc/mole at 25°C. Above 1000 atm the sign of ΔV changes to minus.

Introduction

Recently several workers¹⁻³⁾ have observed that the c. m. c. of aqueous detergent solution increases with increasing pressure and above 1000 atm it begins to decrease at higher pressures. Nevertheless, it is difficult to find a definite conclusion to explain this phenomenon from rather scattered examples. Therefore we⁴⁻⁶⁾ have intended not only to clarify the phenomenon at high pressures but also to elucidate the structure of the micelle. Alkil dodecyl ammonium salts having a different kind of polar group were chosen as samples to know the effect of its structure on c. m. c. at high pressures.

For obtaining the c. m. c. of detergent solution at high pressures the electrical conductivity measurement was performed because of its facility and precision. Dodecyl trimethylammonium chloride (DTAC) and dodecyl benzyldimethylammonium chloride (DBAC) showed a similar behavior with the samples so far investigated by other workers. On the contrary, dodecyl ammonium chloride (DAC) showed an abnormal behavior concerning the specific conductivity at high pressures. The specific conductivity decreases abruptly at a certain high pressure depending on the concentration of DAC. This kind of phenomenon has not been found in any other samples so far investigated. It would be attributed to a certain kind of phase transition i. e. the formation of a new type of micelle at high pressures.

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- 4) J. Osugi and M. Sato, *Preprint of 6th Symposium on High Pressure*, p. 40 (1964)
- 5) J. Osugi and M. Sato, *Preprint of 18th Annual Meeting of Chemical Society of Japan*, p. 154 (1965)
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Experiments

Reagents

DAC: It was prepared by the reaction of dodecylamine with HCl by the method of Ralston *et al*⁷⁾. The crystal obtained was recrystallized from ethanol-ether solution.

DTAC and DTAC: The commercial pure substance was used without further purification.

Apparatus

High pressure vessel: It is manufactured by Kobe Steel Co. Ltd., and its cross section is shown in Fig. 1. The silicone oil was used as pressure transmitting medium. The pressure was calculated by multiplying the measured values of a calibrated Bourdon-type guage by the ratio of the piston area of lower pressure side to higher pressure one.

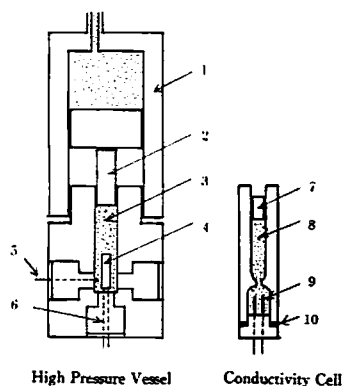


Fig. 1 Apparatus

- | | |
|----------------------|-------------------------|
| 1, intensifier | 6, electrical leads |
| 2, piston | 7, sliding piston |
| 3, silicone oil | 8, sample solution |
| 4, conductivity cell | 9, platinum electrode |
| 5, thermo-couple | 10, nitrile gum packing |

Conductivity cell

It is made of teflon and has a pair of platinized platinum electrode (0.5 cm^2). The sample solution, which was isolated from a silicone oil with a teflon sliding, was compressed through the pressure fluid by means of a high pressure piston.

Electrical conductivity measurement

The low frequency bridge (800cps) (type MY-7) made by Yanagimoto Seisakusho Co. Ltd., was used.

Thermostat

The temperature was controlled at $25 \pm 0.01^\circ\text{C}$ by using liquid paraffin. The temperature of the inside of the high pressure vessel immersed in the thermostat was measured by a thermocouple of iron-constantan.

Results

The specific conductivity of DAC, DTAC, and DBAC was measured at high pressures up to 5000 atm. The concentration range of each detergent was chosen to include its c. m. c. at atmospheric pressure.

7) A. W. Ralston, E. T. Hoffman, C. W. Hoerr and W. M. Selby, *J. Am. Chem. Soc.*, **63**, 1598 (1941)

For example, the concentration of the samples 1, 2 and 3 in Fig. 2 is below c. m. c. at atmospheric pressure, and that of 4, 5 and 6 is above c. m. c.

Concerning the effect of pressure on the specific conductivity, it is shown in Figs. 2, 3 and 4 that the

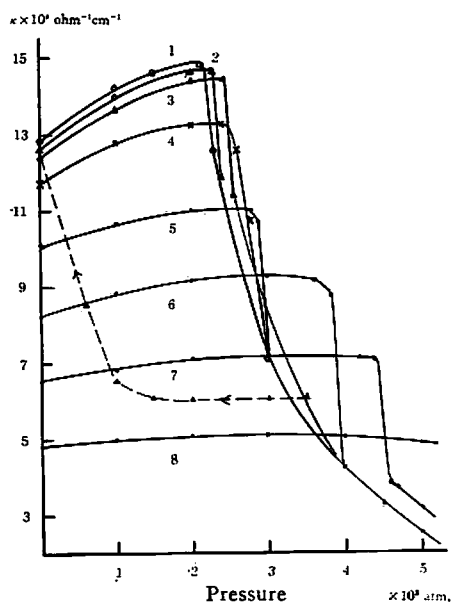


Fig. 2 Specific conductivity of dodecyl ammonium chloride at high pressure

1. 0.021 molal
2. 0.018
3. 0.015
4. 0.013
5. 0.011
6. 0.009
7. 0.007
8. 0.005

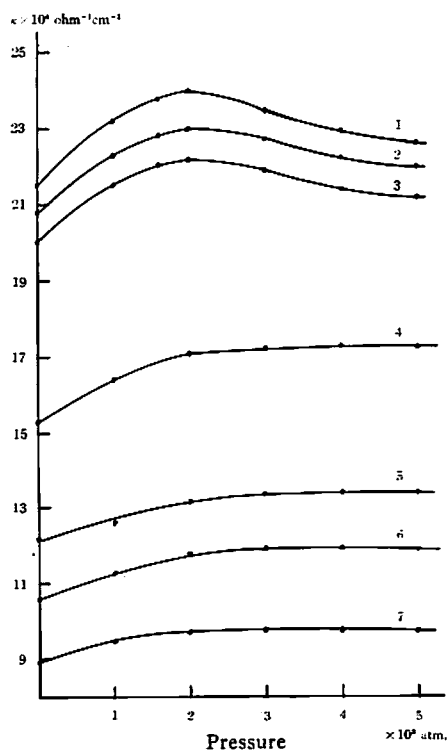


Fig. 3 Specific Conductivity of dodecyl trimethylammonium chloride at high pressure

1. 0.0280 molal
2. 0.0261
3. 0.0243
4. 0.0168
5. 0.0131
6. 0.0112
7. 0.0093

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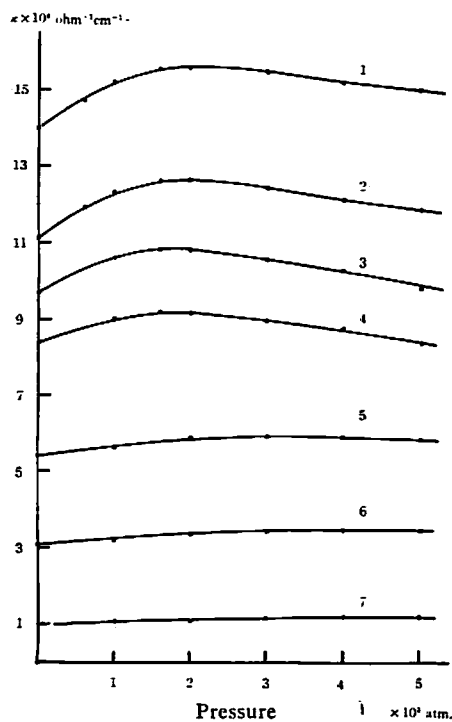


Fig. 4 Specific conductivity of dodecyl benzyl-dimethylammonium chloride at high pressure

1. 0.0271 molal
2. 0.0194
3. 0.0155
4. 0.0126
5. 0.0066
6. 0.0034
7. 0.0010

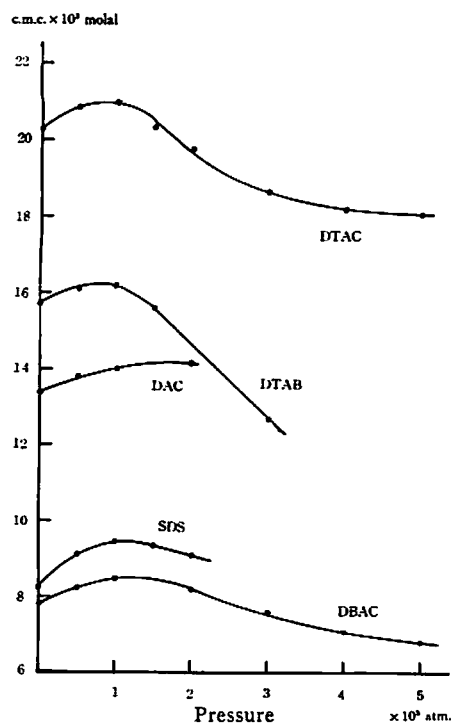


Fig. 5 Variation of c. m. c. with pressure

behavior of DAC is peculiar by comparing that of DTAC and DBAC. The specific conductivity of DAC decreases sharply at certain high pressures depending on the concentration of DAC. The nature of this abnormality will be discussed later. On the other hand, the specific conductivity vs pressure curves of DTAC and DBAC does not show such an abnormality. The samples having a concentration below c. m. c. at atmospheric pressure are not much influenced by pressure. However, the samples having a concentration above c. m. c. at atmospheric pressure show considerable changes by high pressure. Up to about 1500 atm the specific conductivity increases with increasing pressure. Then it begins to decrease monotonously with increasing pressure up to 5000 atm.

By using the results of Figs. 2, 3 and 4, the c. m. c. vs pressure curves are obtained as Fig. 5. As mentioned before, the c. m. c. of DAC could not be obtained above 2300 atm because of its abnormality. Further, the c. m. c. vs pressure curves of sodium dodecyl sulfate (SDS) measured by Hamann¹⁾ and of dodecyl trimethylammonium bromide (DTAB) measured by Tuddenham and Alexander²⁾ are indicated in Fig. 5 as a comparison.

Discussion

Assuming a steady equilibrium between free detergent ions and micellar ions the following equation can be introduced³⁾.

$$nS^+ + (n-z)X^- = M^{z+} \quad (1)$$

where S^+ is a free detergent ion, X^- counter ion, M^{z+} micelle of effective charge $z+$, and n number of S^+ per one micelle ion. Moreover, the partial molal volume change, ΔV , caused by the micelle formation is calculated according to the following equation deduced by Tuddenham²⁾.

$$\Delta V = RT\partial\{(2-z/n)\ln(c. m. c.)\}/\partial p \quad (2)$$

where $(2-z/n)$ stands for the correction factor due to the association of counter ion to micelle.

Although, we have no experimental evidence that the values of n and z are constant at high pressures, it would be reasonable to calculate the values of ΔV at atmospheric pressure from Fig. 5 by using equation (2) and the values of n and z obtained by the light scattering method⁴⁾ by other workers at atmospheric pressure.

Table 1 shows the values of ΔV of DAC, DTAC and DBAC. Besides, ΔV of SDS and DTAB by other workers is indicated as comparison. It is seen from Table 1 that alkyl dodecyl ammonium salts so far investigated have ΔV of small positive value, about $+3\text{cc/mole}$, and that the structure of polar cationic group seems to have no significant influence on the values of ΔV . Further, it is remarkable that the value of ΔV of SDS, anionic detergent, is about thrice a value of cationic detergents having the same number of carbon in hydrocarbon chain.

According to the results of Fig. 5, ΔV of DAC, DTAC and DBAC have positive value at pressures up to about 1000 atm. It could be explained by that hydrated water around free detergent ions is released according to the formation of micelle, so the micellar state is less denser than the free ionic state. There-

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

Table 1 ΔV at atmospheric pressure at 25°C

detergent	$2-z/n$	ΔV cc/mole
DAC	1.86	+2.6
DTAC	(1.8)*	+2.9
DBAC	(1.8)*	+4.4
DTAB	1.79	+3.3**
SDS	1.82	+11***

* assumed value⁹⁾

** present author's calculation

*** Hamann's calculation

fore, the formation of micelle is inhibited by high pressure. Moreover, from the change of the specific conductivity of detergent at high pressures, it is seen that the samples having micellar state even at atmospheric pressure behave like a weak electrolyte i. e. the specific conductivity increases rapidly with increasing pressure. This means that the equilibrium of equation (1) would favor the free ionic state.

Concerning the c. m. c. of DTAC and DBAC, it gradually begins to decrease at high pressures above about 1500 atm. It is meant that the sign of ΔV reverses to minus at this pressure range, though the reason is rather uncertain. If the validity of equation (2) is assumed at such high pressure, it means that the micellar state is again denser than the free ionic state. By considering the same dependency on the pressure of c. m. c. of alkyl dodecyl detergents except DAC, a part of the reason for the inversion of the sign of ΔV could be attributed to the partial freezing of the inside of micelle⁹⁾. In fact, it is known that *n*-dodecane¹⁰⁾ freezes at 1650 atm at 25°C.

For the already mentioned abrupt decrease of the specific conductivity of DAC at high pressures, it seems to suggest the formation of new kind of micelle at high pressures, because, at the inflection point of the specific conductivity, each observed value showed a time dependant decrease until it reaches a finite value. Moreover, the specific conductivity *vs* pressure curve shows a remarkable difference in one cycle of observation by increasing the pressure and then decreasing the pressure. One example of the curve, apparently resembling a hysteresis loop, is indicated in Fig. 2. Further detailed investigation on this point will be performed.

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9) R. S. Bradley, "High pressure physics and chemistry" vol. 2., p. 158, Academic press (1963)

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