THE STATE OF IONIC MICELLES AT HIGH PRESSURES

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A hypothesis proposed earlier by the author, accounting for the unusual behaviour of critical micelle concentrations at high pressures in terms of the pressure-induced freezing of the interiors of the micelles, is shown to be untenable.

In 1962, the author[1] reported the first measurements of the influence of pressure on the critical micelle concentration (c. m. c.) of ionic micelles in aqueous solution. The results (for sodium dodecylsulphate at 25°C) were remarkable inasmuch as, although the c. m. c. initially increased with increasing pressure in accordance with the known relative densities of the monomeric and micellar forms of the salt, that trend unexpectedly reversed at about 1000 atm. Later work by other authors[2–8] on both anionic[4–7] and cationic[2,3,8] micelles has shown that this behaviour is quite general: the c. m. c.'s rise with increasing pressure below about 1000 atm but begin to drop at higher pressures*.

The author[1] proposed a possible explanation of the reversal of behaviour, which has been quoted by some of the later authors[3,4,8,9]; namely, that compression may cause the freezing and consequent contraction of the hydrocarbon cores of the micelles. He pointed out that at 25°C the hydrocarbons n-$C_{16}H_{34}$, n-$C_{12}H_{26}$, n-$C_{10}H_{22}$ and the alcohol n-$C_{12}H_{25}OH$ freeze near 400, 1600, 3000 and 700 atm, respectively, and that the freezing involves a contraction of about 10%. A similar contraction in the hydrocarbon tails of the micelles would be enough to account for the reversal.

It is the purpose of the present note to summarize a number of reasons why the above explanation is now no longer tenable.

First, the author[1] suggested that the hypothesis of freezing could be tested by varying the

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* Rodriguez and Offen[9] have recently reported that the drop of c. m. c. at higher pressures does not appear when the c. m. c. is measured optically instead of conductimetrically. However the presence of a large amount of the indicator, naphthalene, in their micelles (as reflected in the abnormally low value of the c. m. c. at atmospheric pressure) suggests that their experiments should be repeated using a much more immiscible indicator.

1) S. D. Hamann, *J. Phys. Chem.*, **66**, 1359 (1962)
2) R. F. Tuddenham and A. E. Alexander, *J. Phys. Chem.*, **66**, 1839 (1962)
3) J. Osugi, M. Sato and N. Ifuku, *Rev. Phys. Chem. Japan*, **35**, 32 (1965)
4) M. Tanaka, *Yakagaku*, **17**, 148 (1968)
5) M. Tanaka, S. Kaneshina, T. Tomida, N. Noda and K. Aoki, *J. Coll. Interface Sci.*, **44**, 525 (1973)
6) S. Kaneshina, M. Tanaka, T. Tomida and R. Matuura, *ibid.*, **48**, 450 (1974)
7) M. Tanaka, S. Kaneshina, S. Kuramoto and R. Matuura, *Bull. Chem. Soc. Japan*, **48**, 432 (1975)
8) M. Ueno, M. Nakahara and J. Osugi, *Rev. Phys. Chem. Japan*, **47**, 25 (1977)
9) S. Rodriguez and H. Offen, *J. Phys. Chem.*, **81**, 47 (1977)

temperature and hence altering the freezing pressure and the c. m. c. inversion pressure. This was subsequently done[10] and the results are shown in Fig. 1. They are in qualitative agreement with the results of later measurements by Kaneshina *et al.*[6], and show no significant shift of the maximum c. m. c. for a temperature increase of 15°C, which would raise the freezing pressure by about 1000 atm.

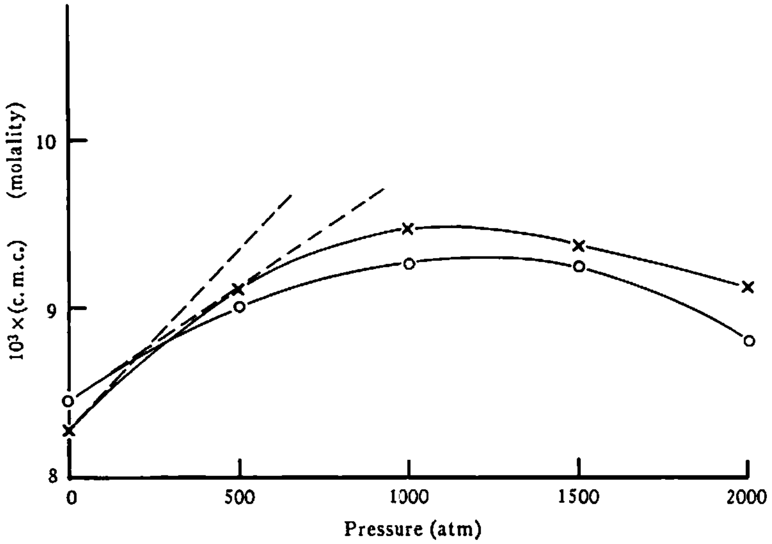

Fig. 1 The influence of pressure on the critical micelle concentration (c. m. c.) of sodium dodecylsulphate in water at 25°C (crosses) and 40°C (circles). The initial slopes, shown as dashed lines, correspond to values of the volume change for micelle formation of +11 cm^3/mol at 25°C and +7 cm^3/mol at 40°C.

Second, the work of Osugi *et al.*[3], of Kaneshina *et al.*[6] and of Ueno *et al.*[8] has shown that the inversion pressure is not sensitive to the structure or chain length of the hydrocarbon part of the micelles, whereas the freezing pressure certainly would be so.

Third, Tanaka *et al.*[11] have found that the partial molar volumes of ionic micelles decrease smoothly with increasing pressure. Total freezing would involve a discontinuity, and partial freezing would involve inflexions.

Fourth, although the freezing pressures quoted in the second paragraph, above, seem almost to *require* that the micelle cores should freeze under pressure, they relate to bulk phases containing enormous numbers of molecules, not to micelles of only tens or hundreds of molecules. Recent molecular-dynamics calculations have shown that the melting temperatures of small clusters of molecules are much lower than the bulk melting points. For example, a cluster of one hundred argon atoms melts at 40 K instead of 84 K[12]. It follows from the principle of corresponding states that the

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[10] S. D. Hamann, unpublished results (1964)

[11] M. Tanaka, S. Kaneshina, K. Shin-no, T. Okajima and T. Tomida, *J. Coll. Interface Sci.*, **46**, 132 (1974)

[12] C. L. Briant and J. J. Burton, *J. Chem. Phys.*, **63**, 2045 (1975)

melting temperature of a cluster of one hundred C_{12} chains could be at least 100°C lower than the normal melting temperature and its freezing pressure at 25°C could lie above 10000 atm instead of being about 1000 atm.

To summarize, although none of the above points is entirely damning on its own, in total they rule out the possibility of pressure-induced freezing of the micelle cores ***under the experimental conditions used so far.*** Tanaka's work[11) has established that the true (macroscopic) explanation of the reversal of behaviour lies in the simple fact that the micelles are more compressible than the dispersed molecules.

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