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DIMINISHED SOLUBILITY OF DODECYLAMINE HYDROCHLORIDE
IN WATER AT HIGH PRESSURES

BY S. D. HAMANN

Experiments in a high pressure optical cell have shown that hydrostatic compression causes a marked decrease in the solubility of dodecylamine hydrochloride in water at 25°C. For instance, a solution that is 60% saturated at atmospheric pressure precipitates crystals of the salt if it is compressed to 2000 atm. It is suggested that this effect is responsible for the anomalous sudden drop in electrical conductivity that Osugi, Sato and Ifuku [*Review of Physical Chemistry of Japan*, 35, 32 (1965)] observed when they compressed solutions of the salt to similar pressures.

Introduction

In a recent paper, Osugi, Sato and Ifuku¹⁾ described some interesting measurements of the effect of pressure on micelle formation in cationic detergent solutions. They reported finding an anomalous abrupt decrease in the electrical conductivity of aqueous solutions of dodecylamine hydrochloride at about 2300 atm, and tentatively attributed it to the formation of a new kind of micelle at high pressure.

It is the purpose of the present note to suggest that the phenomenon arose instead from the precipitation of some of the salt when the solutions became supersaturated under pressure. Osugi, Sato, and Ifuku remarked that the change was time-dependent and that the curve of conductivity against pressure showed an apparent hysteresis loop when the pressure was raised and lowered. Both effects are consistent with the crystallization, under pressure, of a solid phase which is relatively slow to redissolve when the pressure is released. Moreover, density measurements²⁾ have shown that the apparent molar volumes of detergent salts in aqueous solution are generally greater than the molar volumes of their solid forms, and it follows that compression must reduce their solubilities.

Experiments and Discussion

The writer has now examined the phase behaviour of solutions of dodecylamine hydrochloride by observing them visually in a high pressure optical cell maintained at $25 \pm 0.1^\circ\text{C}$. The salt was a specimen that had previously been purified in these Laboratories by careful recrystallization. The solutions were prepared by dissolving weighed amounts of salt in deionized water and were centrifuged to remove any traces of suspended dust. The following is a brief account of the results.

(Received March 1st, 1966)

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

2) K. Shinoda and T. Soda, *J. Phys. Chem.*, 67, 2072 (1963)

In the first experiment a nearly saturated solution of molality $m=0.025$ was rapidly compressed to 2000 atm. Needle-like crystals began to form immediately and grew until they formed a tightly packed mass throughout the whole of the solution. It took many hours for them to redissolve when the pressure was released. In the second experiment an undersaturated solution, $m=0.0157$, was compressed slowly in steps of 200 atm with a ten minute interval between each pressure increment. Crystals began to form at 1600 atm and rapidly spread throughout the solution. The amount of solid formed indicated that the solution must have been considerably supersaturated when crystallization started. In the third experiment a slightly more concentrated solution, $m=0.0174$, was compressed in the same way. Crystallization occurred at 1250 atm, and the crystals failed to redissolve after standing for 14 hours at 1100 atm, or after another 2 hours at 800 atm. Slow solution began at 600 atm, and the photograph (Plate 1) shows some of the partially dissolved salt at that pressure.

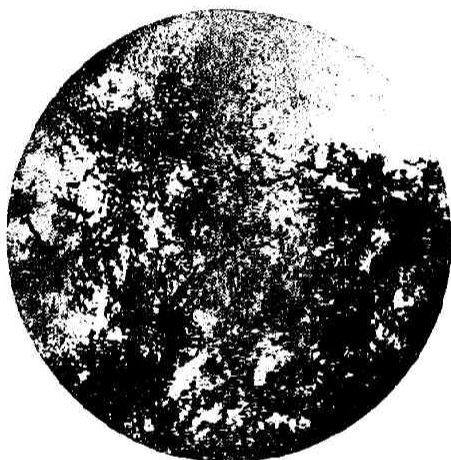


Plate 1 A photograph showing co-existent liquid and solid phases in 0.0174 molal dodecylamine hydrochloride at 600 atm and 25°C

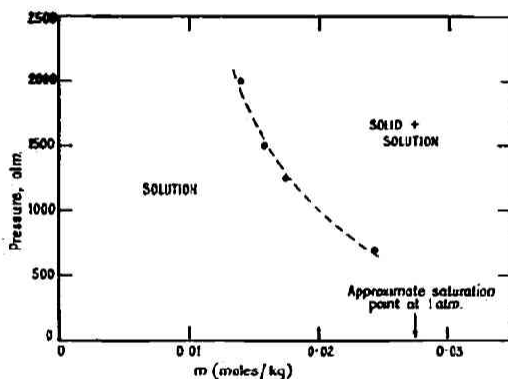


Fig. 1 Onset pressures for the crystallization of dodecylamine hydrochloride from aqueous solutions of molalities m , at 25°C

The results of these and other experiments are shown in Fig. 1, where the pressures for *onset* of crystallization are plotted against the molalities of the solutions at 1 atm. The *equilibrium* pressures were probably lower than these by several hundred atmospheres. The same degree of supersaturation or "superpressing" is indicated by Osugi, Sato and Ifuku's conductivity measurements.

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