a result not apparent in earlier studies.[8] The hydrate $(H_3PO_4)_2 \cdot H_2O$, corresponding to 91.5% $H_3PO_4$, has been reported by Ross and Jones[9] and earlier workers. The premature formation of $H_4P_2O_7$, for example, at compositions below "100% $H_3PO_4$" can be accounted for then if the above

(8) J. H. Lum, J. E. Malowan and C. B. Durgin, *Chem. Met. Eng.*, **44**, 721 (1937).

(9) W. H. Ross and R. M. Jones, THIS JOURNAL, **47**, 2165 (1925); earlier references to the semi-hydrate are given in this article.

hydrate persists in the liquid phase at compositions up to, and then necessarily also slightly exceeding, that corresponding to pure orthophosphoric acid.

The value of "$A$" at 86.5% orthophosphoric acid is in agreement with the more or less constant values observed by Kablukov and Zagvozdkin[5] for acid concentrations ranging from about 6 to 82%.

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# The Binary Systems of Water with Dodecylammonium Chloride and Its N-Methyl Derivatives[1]

BY F. K. BROOME, C. W. HOERR AND H. J. HARWOOD

The systems of dodecylammonium chloride and its N-methyl, dimethyl and trimethyl derivatives with water have been investigated over the entire range of concentration. Each of these systems is characterized by the formation of a hydrate which forms a simple eutectic with water and possesses an incongruent melting point. Superimposed upon these systems are mesomorphic regions indicative of various liquid crystalline orientations. In the primary and secondary salt systems the liquidus curve in dilute solution is altered abruptly by the occurrence of the so-called "Krafft effect" in the region of micelle formation. The liquidus curve of the primary salt is further interrupted by a crystalline transformation at 57.5°, unstable crystal forms have been observed in all four systems. The similarity of these diagrams with those of the soap–water systems has been mentioned.

Recent reports on the influence of N-methylation on the physical properties of dodecylammonium chloride have included studies of solubilities in hexane, benzene and ethanol[2] and electrical conductances in aqueous solution.[3] Since much of the interest in these materials centers in their colloidal and colloidal–electrolytic nature, the studies have been extended to include their binary systems with water. This paper presents the phase diagrams with water of dodecylammonium chloride and methyl-, dimethyl- and trimethyldodecylammonium chlorides.

## Experimental

**Preparation of Materials.**—The salts used in this study are identical with those of the earlier study,[2] in the report of which their preparations have been sufficiently described. The extremely hygroscopic quaternary ammonium chloride was dried *in vacuo* over phosphorus pentoxide and stored in a dry atmosphere. An infrared spectrogram of this salt in chloroform solution showed no absorption in the 3 and 6 $\mu$ regions, demonstrating the absence of water.

In the primary and quaternary salt studies, two preparations of each of these salts were used in several instances. In all these cases, duplicate concentrations gave reproducibility of the observed phase changes within ±0.1°.

Freshly prepared conductivity water was used in this investigation.

**Procedures.**—Most of the data reported herein were obtained on known mixtures of a salt and water sealed into glass tubes. These tubes, by procedure already described extensively,[4,5,6] were examined visually during heating and cooling. Visible phase changes were observed at all the

(1) Presented before the Division of Physical and Inorganic Chemistry at the Chicago Meeting of the American Chemical Society, September, 1950.

(2) F. K. Broome and H. J. Harwood, THIS JOURNAL, **72**, 3257 (1950).

(3) A. W. Ralston, F. K. Broome and H. J. Harwood, *ibid.*, **71**, 671 (1949).

(4) A. W. Ralston, E. J. Hoffman, C. W. Hoerr and W. M. Selby, *ibid.*, **63**, 1598 (1941).

(5) H. J. Harwood, A. W. Ralston, W. M. Selby, *ibid.*, **63**, 1916 (1941).

(6) C. W. Hoerr and A. W. Ralston, *ibid.*, **64**, 2824 (1942).

points plotted on the diagrams. The lines and curves connecting these points represent true reversible equilibria, observable both upon raising and upon lowering the temperature. In general, the transition temperatures of the crystalline phases were reproducible to within ±0.1° below 100° and ±0.2° above this temperature, with the exception of the metastable equilibria of the secondary and tertiary salt systems which are probably accurate only to ±0.5°. The curves representing the unstable systems were obtained by lowering the temperature of a mixture until crystals appeared and then raising the temperature until solution occurred. Maintaining the temperature for a time just below the precipitation point resulted in transformation to the stable form and re-solution only at the higher temperature. In the case of quaternary salt mixtures in the neighborhood of the eutectic composition, the transformation was exceedingly slow, extreme conditions such as Dry Ice temperatures overnight being used to effect the transformation. Phase boundaries among the liquid–crystalline phase were reproducible within about ±0.2° below 100° and ±0.5° above this temperature.

At high salt concentrations, particularly in the case of trimethyldodecylammonium chloride, the high temperatures necessary to produce isotropic solutions result in excessive decomposition. Therefore, in some cases it was impossible to obtain perfect homogenization of the tube contents before observations were made. Satisfactory mixing, as judged by the reproducibility and reasonableness of results, was obtained by subjecting the tubes and contents to ultrasonic vibrations.

The liquidus and solidus curves of the crystalline systems at concentrations below those of the eutectics were verified by means of cooling and heating curves. These curves were obtained with a platinum resistance thermometer in conjunction with a Mueller bridge (Leeds and Northrup). The temperatures at which ice or the eutectic mixtures froze and melted agreed within ±0.05° and were reproducible well within these limits.

A number of mixtures of amine salt with water were examined on an electrically heated stage under a polarizing microscope ($\times 420$). Concentrations of amine salt were so chosen that all the regions observed macroscopically below 100° could be verified microscopically upon heating and cooling. The existence of the various regions was further proved by allowing dilute solutions to evaporate at constant temperature, thereby traversing the various regions of the diagrams isothermally. The decomposition temperature of the hydrate of dodecylammonium chloride was established microscopically within ±0.1°.

## Results and Discussion

Figures 1–4 present the systems of the four salts with water. (Portions of Fig. 1 were taken from an earlier report.[4]) Mole-per cent. plots are not used since they condense the regions of low salt concentrations excessively. In all the diagrams, the symbols I, II, III, IV, V and VI indicate the same types of phases or mixtures of phases. Area I is isotropic, relatively non-viscous liquid. Area II consists of solid hydrate and liquid, area II' of solid hydrate and liquid crystals and area II" of solid hydrate and a different form of liquid crystals. Area III, which is very small in the primary and secondary salt systems, comprises ice and liquid, area III' ice and liquid crystals and area III" ice and a different form of liquid crystals. Area IV is a mixture of ice and crystalline hydrated salt, area V comprises a mixture of solid hydrate and anhydrous salt, and area VI is made up of anhydrous salt and liquid crystals. In all figures the letters have identical meanings, describing the eutectic (E) between water and hydrate, the incongruent melting point
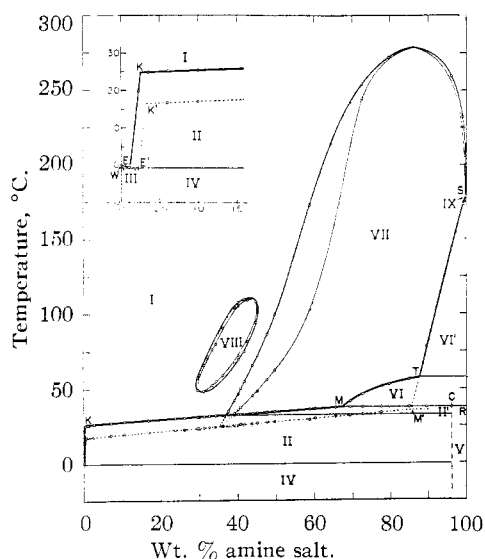


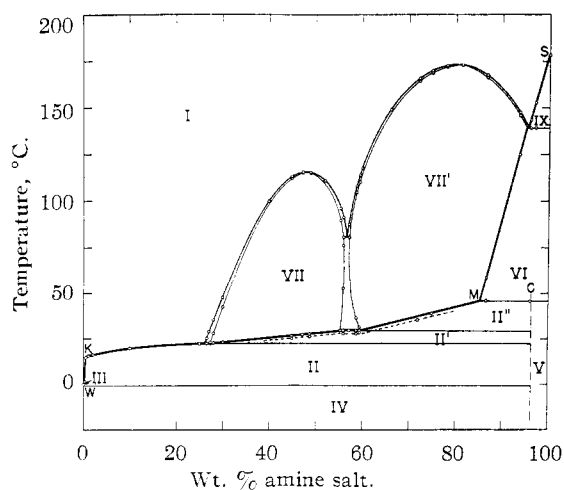Fig. 3.—The system dimethyldodecylammonium chloride-water.
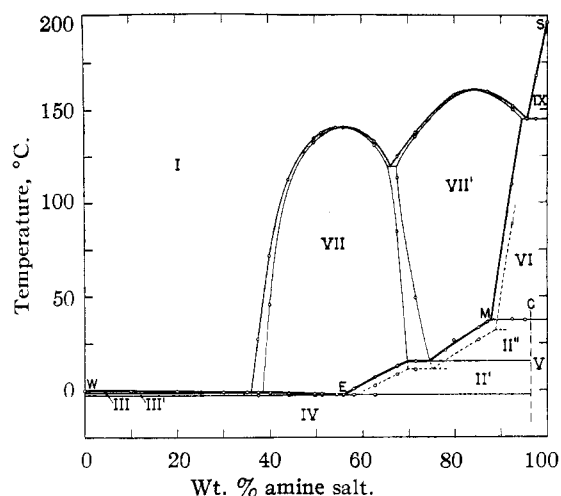


Fig. 1.—The system dodecylammonium chloride–water.



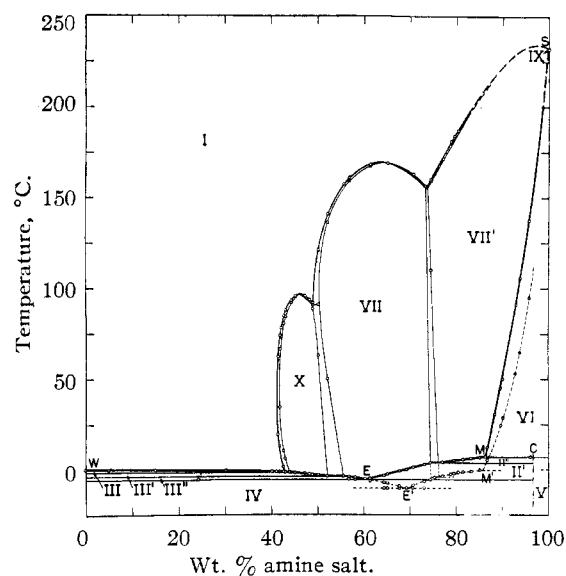Fig. 2.—The system methyldodecylammonium chloride-water.



Fig. 4.—The system trimethyldodecylammonium chloride-water.

(M) of the hydrate, the submerged maximum (C) of the hydrate solubility curve and the freezing points of water (W) and the anhydrous salt (S). In the systems of the primary and secondary salts (Figs. 1 and 2), the so-called "Krafft effect" produces the abrupt change of direction of the curves at K and the succeeding relatively flat portion with increasing concentration. This effect is caused by entrance of the solubility curve into the region of micelle formation.[7] The point K is absent from the tertiary and quaternary ammonium salt diagrams (Figs. 3 and 4) simply because these salts are much more soluble in water in regions of low concentration. A plot of critical micelle concentration against temperature in these cases would be interrupted by the portion of the phase diagram along which ice separates from solution. Breaks in the liquidi corresponding with these intersections could not be detected.

In all four systems the hydrates have been repre-

(7) D. N. Eggenberger and H. J. Harwood, THIS JOURNAL, 73, 3353 (1951).

sented as composed of two moles of amine salt and one of water. The dodecylammonium chloride hydrate was isolated by slow crystallization from aqueous solution. Analysis of the crystals[8] gave 96.05% $C_{12}H_{25}NH_2Cl$. The calculated value for the hemihydrate is 96.10%. The hemihydrate decomposes abruptly at 37.0° upon heating, along the line MR in Fig. 1, and effloresces at room temperature. Hydrates of the other salts were not actually isolated.

The point T of Fig. 1, at 57.5°, is unique with the primary salt. This enantiotropic transition temperature was located in an earlier investigation[2] from solubility measurements in organic solvents. Thus, the line EKM represents the solubility of the hydrate of the primary salt in water, MT represents the solubility of that form of the anhydrous salt stable below 57.5°, and TS the solubility of that form stable above this temperature. The curve E'K'M' represents the solubility of a metastable form of the hydrate, where M'T represents that of the anhydrous salt below its transition temperature. It will be noted that in several instances dotted lines (such as M'T in Fig. 1) and isotherms have been included in the diagrams without experimental points. Such transitions were not observable by the experimental procedures used. Their location was based upon the configuration of the systems and they are included in order that the systems be consistent with phase-rule theory. Unstable forms exist in all four systems and have been indicated by broken lines over the ranges in which they were identified.

Area VII of Fig. 1 is a homogeneous region consisting of material in the mesomorphic state. This material breaks down along the upper boundaries of the area to give a heterogeneous mixture of mesomorph and liquid which coalesces to form the isotropic liquid of area I upon further heating. The heterogeneous area to the left is bounded at its lower limit by an isotherm which extends to the composition of the hydrate.

The insular region, area VIII, is a thixotropic gel which examination with the polarizing microscope shows to be in the mesomorphic state. This area is likewise bounded at right and left by heterogeneous regions.

Areas VII and VII' in the secondary salt system (Fig. 2) are rather fluid, mesomorphic regions ap-

parently existing in different liquid–crystalline orientations as evidenced by their behavior toward polarized light. The areas VII in the tertiary and quaternary ammonium salt systems (Figs. 3 and 4) are similar to area VII of Fig. 2. On the other hand, areas VII' in Figs. 3 and 4 are rigid, isotropic jellies which become birefringent when forced to stream, as by pressure applied to the cover glass on a microscope preparation. In each of the systems in Figs. 2, 3 and 4 the homogeneous areas VII and VII' are separated by heterogeneous regions consisting of mixtures of the phases of these two areas. Likewise, these areas are bounded by heterogeneous mixtures of mesomorph and liquid in the regions adjacent to area I. As in the corresponding regions of the primary salt diagram (Fig. 1), all these heterogeneous regions are bounded at their lower limits by isotherms.

Area IX, which exists in all the systems but is small in the primary and quaternary ammonium salt diagrams, consists of a two-phase mixture of liquid and anhydrous salt. Its lower limit is an isotherm along which the liquid portion of this mixture is converted to liquid crystals, and its upper limit is the solubility curve of the salt.

In the quaternary ammonium salt system (Fig. 4), there appears an area not identified in any of the other systems. Area X comprises a clear, rigid, isotropic jelly bounded by two-phase regions.

The similarity between these systems and McBain's soap diagrams[9] is to be noted. Regions VII and VII' correspond to the so-called "middle" and "neat" soaps, and the solid material of area VI corresponds to the "curd-fiber" phase. In contrast to the soap–water systems, however, the systems of these cationic colloidal electrolytes do not undergo the numerous changes referred to as "waxy," "super-waxy" and the like. And with the exception of the transition of dodecylammonium chloride at 57.5°, no phase changes were encountered in any of the anhydrous amine salts investigated. It is probable that truly anhydrous soaps would exhibit no changes either,[10] and that the regions indicated in the numerous soap–water diagrams would disappear at a finite, although small, distance from the 100% soap line.

(8) A. W. Ralston and C. W. Hoerr, Ind. Eng. Chem., Anal. Ed., 16, 459 (1944).

(9) R. D. Vold, R. Reivere and J. W. McBain, THIS JOURNAL, 63, 1293 (1941).

(10) F. H. Stross and S. T. Abrams, ibid., 72, 3309 (1950).