

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

Studies on High Molecular Weight Aliphatic Amines and Their Salts. IX. The Behavior of Various Salts of Dodecylamine in Water, Ethanol and Benzene

BY C. W. HOERR AND A. W. RALSTON

Previous papers in this series have presented various aspects of the behavior of the normal primary aliphatic amine hydrochlorides and hydroacetates in water,¹⁻⁴ and in ethanol and benzene.⁵ These studies have shown that in water these salts are colloidal electrolytes, similar in their behavior to compounds in which the paraffin chain is in the anionic portion of the molecule. In dilute solution they act as simple, completely dissociated, uni-univalent electrolytes, while at certain concentrations dependent upon the length of the paraffin chain, a colloidal transformation results from the formation of micelles. With ethanol and with benzene, the amine salts form simple eutectic systems in which the eutectic composition is located in the region of very small concentration of amine salt.

This investigation is carried further by the preparation of a wide variety of salts of dodecylamine. While this paper is primarily a report of the solubilities of these salts in water, ethanol and benzene, a study of the phase changes of several of the salt-water systems has been included, together with a study of the state of some of the salts in solution, as indicated by their effects in depressing the freezing point of water and that of benzene.

Preparation of Materials.—The dodecylammonium chloride and the acetate were of the same lots which were used in previous experiments, and their preparations and constants have been reported.^{1,3,5} The preparations of the following salts have not been reported elsewhere. These salts were prepared by adding equimolar portions of the appropriate acids to dodecylamine in the most satisfactory solvent, as noted below.

Dodecylammonium *n*-propionate and dodecylammonium *n*-butyrate were prepared in the manner of the acetate,² the propionate by repeated recrystallizations from ethyl ether and benzene, alternately, and the butyrate from petroleum ether (Skellysolve "F," b. p. 30–60°), until their melting points were constant. The melting point of the propionate was 56.7–56.9° and that of the butyrate was 41.0–41.2°.

Dodecylammonium formate, bromide and iodide were prepared by the method used for the chloride¹ with ben-

zene as the solvent to facilitate the removal of the water introduced by the addition of the acids. No melting points could be obtained for these salts since they decompose at temperatures above 160°. Dodecylammonium formate transforms above 63° to a firm semi-solid liquid crystalline state.

Dodecylammonium acid sulfate and primary dodecylammonium phosphate were crystallized from 95% ethanol. Since dodecylammonium normal sulfate and secondary dodecylammonium phosphate are not appreciably soluble in any of the usual solvents, these salts were refluxed with ethanol for several hours, washed repeatedly with hot water and with ethanol, and finally with hot benzene. No melting points could be obtained for either of the sulfates or the phosphates since they decompose on heating above 250°. Attempts to prepare *t*-dodecylammonium phosphate were unsuccessful.

Dodecylammonium dodecylcarbamate was prepared in this Laboratory by Dr. F. M. Garland. Pure, dry carbon dioxide was passed into liquid dodecylamine at about 30°. Measurement by means of a gas buret of the quantity of carbon dioxide which reacted indicated that two moles of amine combine with one mole of carbon dioxide. This compound was purified by repeated crystallization from 95% ethanol. It melts at 92–93°, and decomposes at 98° to dodecylamine and carbon dioxide.

The secondary and tertiary amine salts were prepared in this Laboratory by Dr. W. O. Pool. Primary dodecyl alcohol (133 g.) was refluxed with resublimed iodine (97 g.) and red phosphorus (7.2 g.) for one hour at 170°. The dodecyl iodide (b. p. 118–120° at 0.7 mm.) was removed from the mixture by solution in ethyl ether and purified by fractional distillation under reduced pressure. The iodide (184 g.) was then heated with methylamine (635 g. of methanol solution containing 13.6 g. methylamine per 100 ml.) in a bomb for eight hours at 135 ± 5°. Excess methanol and methylamine were removed by distillation, and the *N*-methyl dodecylamine was purified by fractionation *in vacuo*. Its boiling point was 88–89° at 1 mm. The hydrochloride of this amine was prepared in the manner of the corresponding primary salt. It melts with decomposition at about 180°, which agrees with a recent observation.⁶

N-Dimethyldodecylamine was prepared by the same method as was used for the corresponding secondary amine, except that a methanol solution of dimethylamine was used. The boiling point of the tertiary amine was 87–88° at 0.9 mm. The hydrochloride and hydroacetate of this amine were prepared by the methods used for the corresponding primary salts, the hydrochloride melting at 170–171° and the hydroacetate at 38.8–39.0°.

The water used in these experiments was freshly distilled conductivity water. The ethanol was commercial "absolute" (99.4% by weight) diluted to 95.0% by weight, ex-

(1) Ralston, Hoffman, Hoerr and Selby, *THIS JOURNAL*, **63**, 1598 (1941).

(2) Ralston, Hoerr and Hoffman, *ibid.*, **63**, 2576 (1941).

(3) Ralston, Hoerr and Hoffman, *ibid.*, **64**, 97 (1942).

(4) Ralston and Hoerr, *ibid.*, **64**, 772 (1942).

(5) Harwood, Ralston and Selby, *ibid.*, **63**, 1916 (1941).

(6) Westphal and Jerchel, *Ber.*, **73B**, 1002 (1940).

cept where other dilutions are noted below. The ethanol concentration was determined by measurement of its density at each dilution with a 25-ml. pycnometer, and interpolation of these values with those from the "International Critical Tables."⁷ The benzene was Baker c. p. thiophene-free grade and was dried over sodium wire.

Apparatus and Procedure.—The experimental procedures were essentially those used in the previous investigations of this series. Visual observations were made by the synthetic method first proposed by Alexejew.⁸ The samples were prepared in small glass tubes and rotated in a water-bath with the apparatus and by the procedure described elsewhere.^{1,5} Temperatures were measured with a calibrated thermometer which was graduated in 0.1° intervals. The temperatures of solution of the amine salts investigated were reproducible to $\pm 0.1^\circ$, and are, in general, considered accurate within $\pm 0.2^\circ$.

Transition temperatures of the system dodecylammonium acetate-water below approximately 80° were determined by analysis of cooling curves. These were obtained by carefully controlled cooling of 5–7 g. samples contained in test-tubes (1.5 × 15 cm.) immersed in a bath (800 ml.) of light mineral oil (acetone was used as the bath for sub-zero temperatures). After preliminary heating to homogeneity, the acetate-water samples were allowed to cool slowly while being agitated with a small "Chromel" wire stirrer. The temperature of the bath was at no time more than 2° below that of the sample. Undercooling, in general, did not occur. Temperatures of the samples were read with the calibrated thermometer. The transition temperatures of this system are considered to be accurate to $\pm 0.5^\circ$ above 80°, while below this temperature they are probably accurate within $\pm 0.2^\circ$.

The depression of the freezing points of water and of benzene by several of the salts was measured by means of a Beckmann thermometer which had been calibrated by the National Bureau of Standards, and the temperatures obtained were considered accurate to $\pm 0.001^\circ$.

Various compositions of dodecylammonium acetate in water were examined microscopically with polarized light to confirm the preliminary gross visual observations of the nature of the phases which were present.

Results

The Acetate-Water Systems.—A preliminary study of the system dodecylammonium acetate-water has been reported previously.² In the light of recent investigation of the higher amine-water systems,⁹ this acetate-water system was studied further, and the complete temperature-concentration diagram is shown in Fig. 1. On this diagram,

(7) "International Critical Tables," 1929, Vol. III, p. 117.

(8) Alexejew, *J. prakt. Chem.*, **133**, 518 (1882); *Bull. soc. chim.*, **38**, 145 (1882).

(9) Ralston, Hoerr and Hoffman, *THIS JOURNAL*, **64**, 1516 (1942).

A represents the freezing point of dodecylammonium acetate (69.3°) and K that of water. Area 1 is clear, isotropic solution. Two hydrates are found, a tetrahydrate (m. p. 129.0°) and an eicosahydrate (m. p. 86.0°).

The eutectic between dodecylammonium acetate and its tetrahydrate is represented by B. Areas 2 and 3 are two phase mixtures. Area 5 is a region of microscopically homogeneous material in a mesomorphic state. This region is analogous to the solid solutions of metallic systems and is physically identical with the corresponding phases of the amine-water systems,⁹ with reference to which a sufficiently thorough discussion has been presented. Area 4 consists of a mixture of acetate crystals and the solid solution phase of concentration on curve EN. A eutectoid between the acetate and water is represented by N. Area 6 consists of a mixture of crystals of these components. F represents a eutectic between the

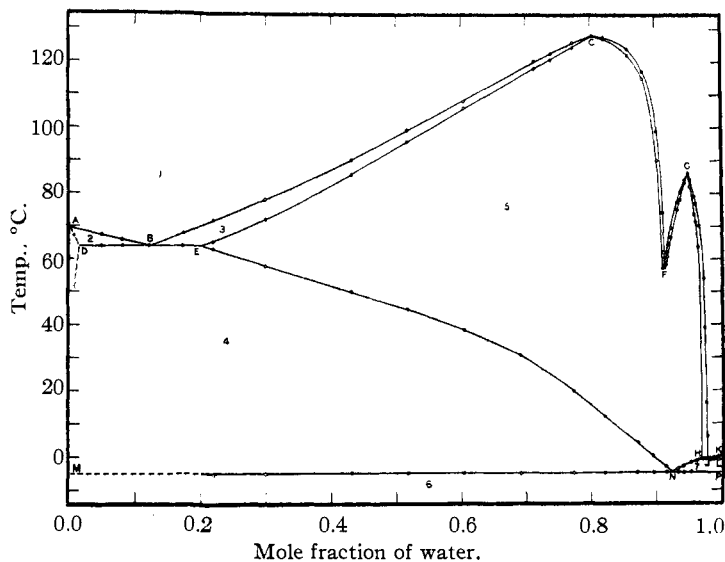


Fig. 1.—The system dodecylammonium acetate-water.

tetrahydrate and the eicosahydrate. After passing through a narrow two phase region upon cooling, samples containing mixtures of these two hydrates become physically identical with other samples in area 5. J represents a eutectic between the eicosahydrate and water.

The broken lines at the left of Fig. 1 represent the existence of a region of solid solution, which was indicated by observation, though not verified by direct measurement.

Other Solubilities in Water.—Dodecylammonium formate and *n*-propionate and *N*-dimethyldodecylammonium acetate exhibit be-

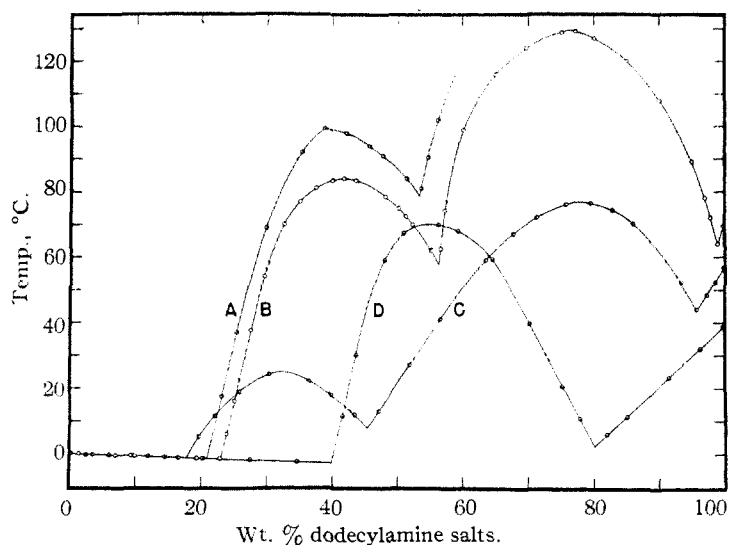


Fig. 2.—Liquidus curves of dodecylamine salts in water: dodecylammonium formate, A; acetate, B; propionate, C; N-dimethylammonium acetate, D.

havior with water similar to that of the acetate. Since the latter system has been described sufficiently, only the liquidus curves of these salts are shown graphically in Fig. 2. Due to thermal instability of the formate, this system was not investigated beyond approximately 60%.

Study of these systems shows the presence of the following hydrates. The formate forms at least one hydrate, an eicosahydrate (m. p. 99.6°). The propionate, like the acetate, forms two hydrates, a tetrahydrate (m. p. 77.0°) and a triacontahydrate (m. p. 24.8°). N-Dimethyldodecylammonium acetate forms one hydrate, a dodecahydrate (m. p. 70.0°).

While it has not been thoroughly investigated, the butyrate-water system is qualitatively similar to the system octadecylammonium acetate-water.² Above 33°, the butyrate system exists as two conjugate solutions over practically the entire range of concentration, similar to the behavior of the octadecylamine salt. In the case of dodecylammonium butyrate, the region of isotropic solution exists over a much smaller range of concentration than does the corresponding region of the octadecylamine salt system.

Figure 3 shows the solubilities of dodecyl-

ammonium bromide and iodide, primary dodecylammonium phosphate, N-methyldodecylammonium chloride and N-dimethyldodecylammonium chloride, together with the curve which has been reported for dodecylammonium chloride.¹ All of these salts pass through the same phase changes as does the chloride. In all cases, except that of N-dimethyldodecylammonium chloride, there is an abrupt change in the solution temperature at approximately 0.39%. In the case of the bromide, a metastable form precipitates from solution upon cooling, as indicated by the broken line in Fig. 3. This behavior recalls that of dodecylammonium chloride.¹ No metastable compound formation by the other salts was observed.

From the freezing point data, the osmotic coefficient g was calculated for dodecylammonium formate, acetate and propionate, and for the hydroacetate and hydrochloride of N-dimethyldo-

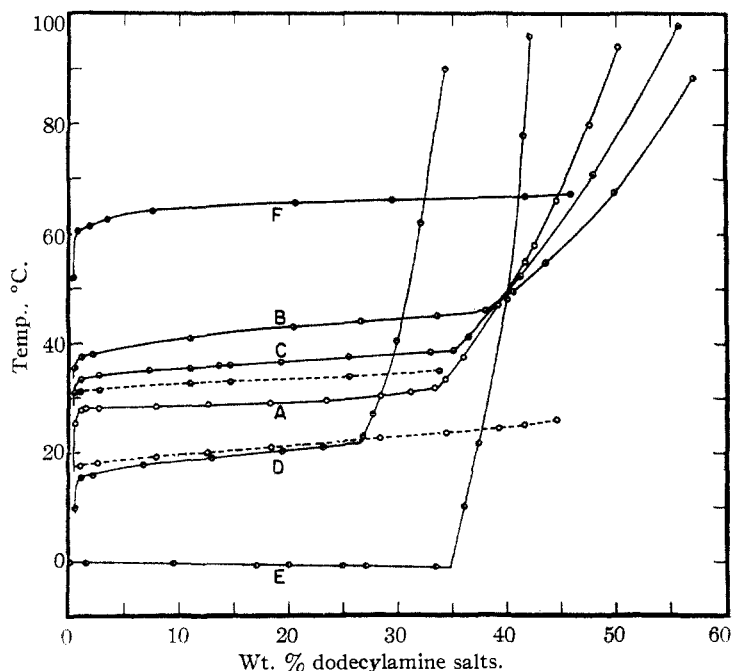


Fig. 3.—Solution temperatures of dodecylamine salts in water: dodecylammonium chloride, A; iodide, B; bromide, C; N-methylammonium chloride, D; N-dimethylammonium chloride, E; primary dodecylammonium phosphate, F. The broken lines refer to the corresponding metastable modifications.

decylamine. These values are plotted against the square root of the molality ($\sqrt{N_w}$) in Fig. 4.

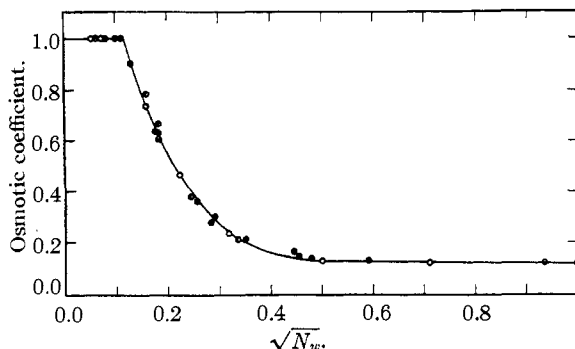


Fig. 4.—Osmotic coefficients of dodecylamine salts in water: \otimes formate, \circ acetate, \bullet propionate, \ominus N-dimethylammonium chloride, \ominus N-dimethylammonium acetate.

It can be seen from Fig. 4 that the values for the osmotic coefficients of all of the salts investigated fall on the same curve, within experimental error. Up to approximately 0.013 molal these salts behave as simple, completely dissociated, uni-univalent salts, as shown by the fact that their osmotic coefficients are 1.0 in this range. At 0.013 molal, the values of g decrease abruptly, indicating the formation of micelles in these solutions. This molality agrees with the value of the critical concentration for the formation of micelles which has been reported^{3,4} for the dodecylammonium ion.¹⁰ The interesting fact to be noted in this connection is that the values of the osmotic coefficients of the N-dimethyldodecylamine salts fall on the same curve as the primary dodecylamine salts. Evidently, in the case of these salts at least, N-substitution by methyl groups has no apparent effect upon the concentration at which micelles are formed.

Solubilities in Ethanol.—In Figs. 5 and 6 are shown the solubilities of the dodecylammonium halides, the acetate series, the dodecylcarbamate, the primary phosphate and the acid sulfate in 95.0% ethanol.

In preliminary study of dodecylammonium acetate it was observed that the solubility of this salt was increased by the dilution of ethanol with water. To investigate this further, a number of samples containing 50.0% dodecylammonium

(10) While this value was reported in terms of molarity, the values of molality and molarity are, for all practical purposes, equal in these dilutions.

acetate were prepared in various dilutions of ethanol in small sealed glass tubes, and the temperatures at which solution occurred were determined by visual observation. The results of this experiment are shown graphically in Fig. 7; 41% aqueous ethanol gave the lowest solution temperature observed for a 50.0% mixture of dodecylammonium acetate-solvent. Minimum solution temperatures of other concentrations of this salt occur at approximately $45 \pm 5\%$ ethanol.

Solubilities in Benzene.—The solubilities of the dodecylammonium halides in anhydrous benzene are shown in Fig. 6, and Fig. 8 shows those of dodecylammonium formate, acetate, propionate, butyrate and dodecylcarbamate in the same solvent. The propionate and butyrate (and no doubt the other salts also) form simple eutectics with benzene. In the case of the butyrate, the eutectic is located at 3.6%, and that of the propionate occurs at 0.75%, while those of

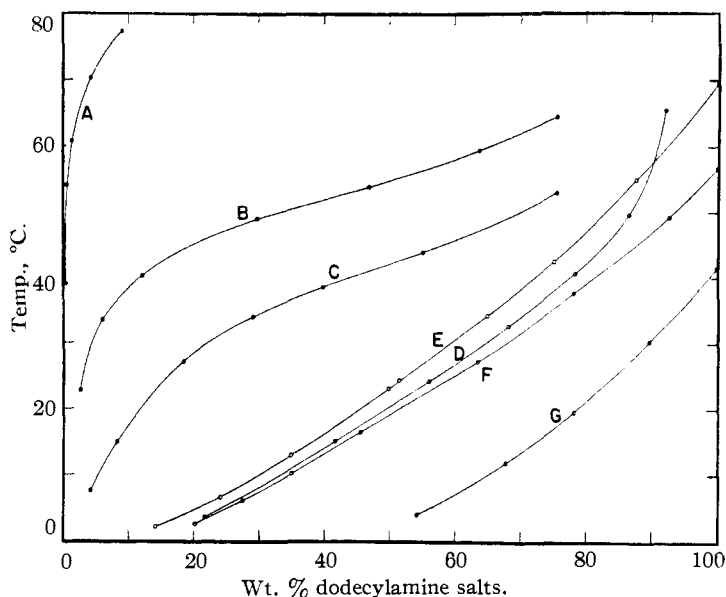


Fig. 5.—Solution temperatures of dodecylamine salts in 95.0% ethanol: primary dodecylammonium phosphate, A; dodecylammonium dodecylcarbamate, B; dodecylammonium acid sulfate, C; dodecylammonium formate, D; acetate, E; propionate, F; butyrate, G.

the acetate and formate occur at considerably greater dilutions.

The lowering of the freezing point of benzene by dodecylammonium butyrate was measured accurately up to the concentration of the eutectic (3.6%). The apparent molecular weight of the butyrate was calculated from the amount of the freezing point depression at each concentration measured. The results are shown graphically in

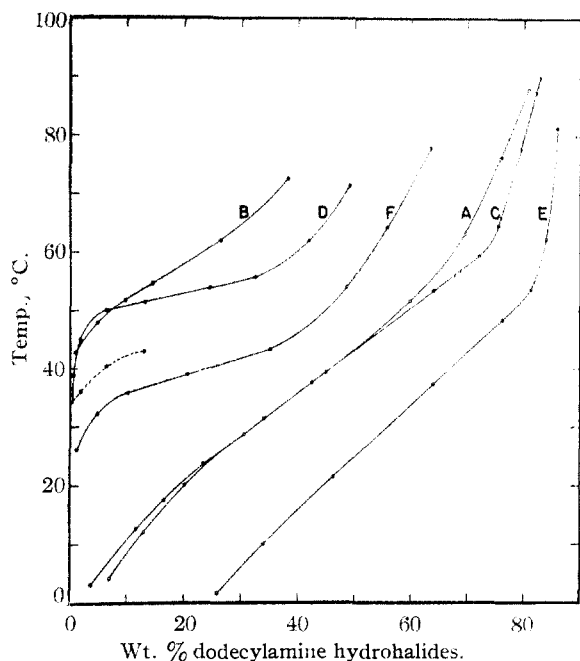


Fig. 6.—Solution temperatures of dodecylamine hydrohalides in 95.0% ethanol and in anhydrous benzene: dodecylammonium chloride in ethanol, A, and in benzene, B; bromide in ethanol, C, and in benzene, D; iodide in ethanol, E, and in benzene, F. The broken line refers to the metastable modification of the bromide in benzene.

Fig. 9 as the ratio of apparent to true molecular weight (M/M_0) against the square root of the molality ($\sqrt{N_{30}}$). At approximately 0.1 molal, M/M_0 approaches a value of 2.0. A few measurements of the effects of the propionate upon the freezing point of benzene showed that its M/M_0 values fall on the curve for the butyrate.

The increase of the apparent molecular weight of dodecylammonium butyrate in benzene indicates that there is probably some degree of molecular association. Figure 9, however, cannot be interpreted literally to demonstrate that double molecules exist in solution, even though the M/M_0 values approach a value of 2.0 in higher concentrations, since, in the derivation of the equations involved, the solutions were assumed to be ideal, and certain pertinent factors have been omitted. Moreover, it has been proved with reasonable certainty that the values obtained by this method are actually the molecular weight of the solute in the vapor

phase.¹¹ However, it can be assumed safely that if associated molecules exist in the vapor, they

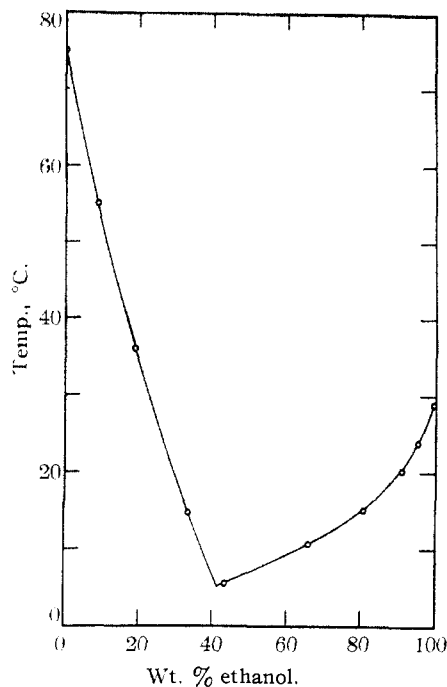


Fig. 7.—Solution temperatures of 50.0% dodecylammonium acetate in aqueous ethanol.

also occur in the solution which is in equilibrium with it, though the extent of the association in the

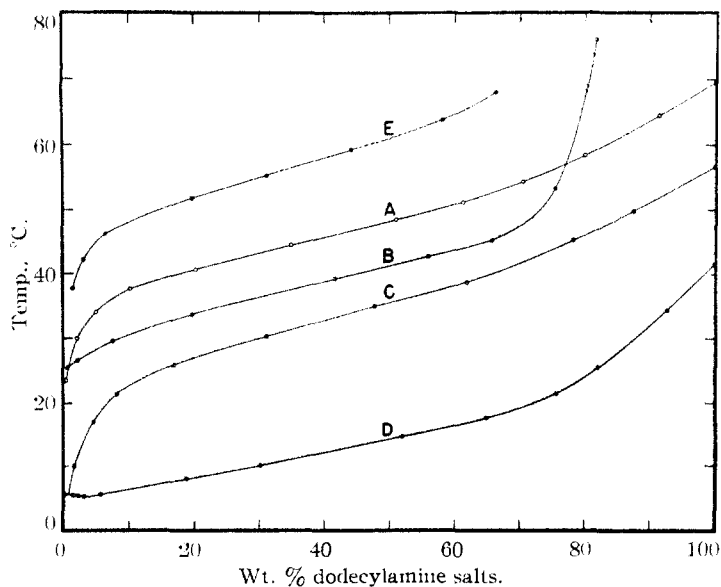


Fig. 8.—Solution temperatures of dodecylamine salts in anhydrous benzene: dodecylammonium acetate, A; formate, B; propionate, C; butyrate, D; dodecyl carbamate, E

latter case is problematical. At any rate, molecu-

(11) Peterson and Rodebush, *J. Phys. Chem.*, **32**, 709 (1928).

lar association of dodecylammonium butyrate to some extent in benzene is evidenced by the data presented.

Further evidence of molecular association is indicated by the rather irregular displacement of the solubility curves of dodecylamine salts toward the ethanol and benzene axes. Similar behavior of the higher fatty acids in benzene has been attributed¹² to molecular association in solution.

Summary

1. The solubilities of dodecylammonium formate, acetate, *n*-propionate, *n*-butyrate, chloride, bromide, iodide, dodecylcarbamate, primary and secondary phosphates and acid and normal sulfates, N-methyldodecylammonium chloride and N-dimethyldodecylammonium chloride and acetate in water, ethanol and benzene have been determined.

2. The phase changes of the water systems of dodecylammonium formate, acetate, propionate and N-dimethyldodecylammonium acetate have been investigated, and the hydrates formed by these salts are reported.

(12) Powney and Addison, *Trans. Faraday Soc.*, **34**, 625 (1938).

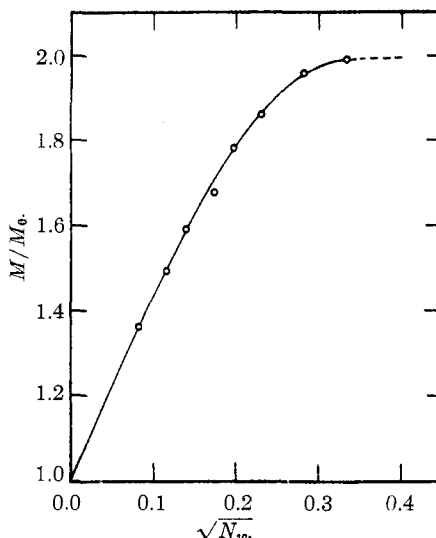


Fig. 9.—Molecular weight of dodecylammonium butyrate in benzene solutions.

3. The colloidal nature of aqueous solutions of these salts has been demonstrated by a study of their osmotic coefficients.

4. Molecular association of dodecylammonium butyrate in benzene has been discussed.

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RECEIVED JUNE 24, 1942

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Dipole Moment, Induction and Resonance in Nitroethane and Some Chloronitroparaffins

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Recent investigations¹ have shown an increase of moment of 0.21–0.23 from nitromethane to α - and β -nitropropane and 2-methyl-2-nitropropane, presumably because of the effect of induction upon the α - and β -carbons, since branching of the carbon chain did not increase the moment appreciably above that of the straight-chain nitropropane. One would, therefore, expect the moment of nitroethane to be close to those of the nitropropanes and nitrobutanes. This appeared to be true in the earlier measurements of Groves and Sugden,² who found 3.58, 3.57 and 3.55 for nitroethane, α -nitropropane and α -nitrobutane, values barely distinguishable from their value 3.54 for nitromethane. As this discrepancy between the two sets of investigations left a slight possibility of further increase of moment and, hence, of inductive effect, from nitroethane

to the propanes, it seemed desirable to make a careful redetermination of the moment of nitroethane. This has been done, together with measurements upon three chloronitroparaffins, from which conclusions as to induction effects may be drawn. At the same time, measurements upon certain previously measured substances have been carried out as a check upon the absolute accuracy of the determinations.

Preparation and Purification of Materials

Carbon Dioxide.—The gas was taken from a cylinder of commercial material, passed through a tube containing eight-mesh calcium chloride and used without further purification.

Benzene.—The material used had been purified by Dr. P. F. Oesper for use in solution measurements and had been dried over sodium wire.

***n*-Octane.**—This hydrocarbon was supplied as a part of the American Petroleum Institute Pure Hydrocarbon Program. It was prepared and/or purified at the Pure Hydro-

(1) Wiswall and Smyth, *J. Chem. Phys.*, **9**, 356 (1941).

(2) Groves and Sugden, *J. Chem. Soc.*, 158 (1937).