aliphatic compounds, both in the values of $1/n$ and in the amounts adsorbed.

While the difference in $1/n$ for the representative carboxylic acids (acetic, benzoic) is not large, the difference becomes much greater when amino groups are introduced; for whereas among aliphatic acids the $1/n$ values are increased by the presence of polar groups, the effect of these groups when placed on the aromatic nucleus is to *lower* the $1/n$ values. The difference in $1/n$ for alanine and phenylalanine is most striking, and illustrates the influence of the benzene nucleus on adsorption.

The relation between the amounts of adsorption and the trend in $1/n$ values is opposite in aromatic compounds to that found among the aliphatic compounds.

The adsorption data for various nutrilites is as varied as might be expected on the basis of the structures of the nutrilites themselves.

Calcium pantothenate, β-alanine, thiamin hydrochloride and inositol are all non-aromatic compounds with several polar groups. Their $1/n$ values are high (above 0.6) in accordance with the previous discussion. The aromatic compounds nicotinic and *p*-aminobenzoic acids and pyridoxin hydrochloride have low $1/n$ values (below 0.4). Biotin, the structure of which is unknown, on this basis would be expected to be non-aromatic ($1/n = 0.69$), provided of course that the extrapolated curve is valid over the extremely wide range for which as yet no experimental data are available.

It is worthy of note that the adsorption data for several of the nutrilites follow the Freundlich equation through extremely wide concentration ranges. By using microbiological tests it has been possible in some cases to measure adsorption from solutions far more dilute than has hitherto been possible in dealing with organic compounds. The application of the Freundlich equation through a wide range is somewhat contrary to results obtained with certain other substances studied within a much narrower range.

Summary

1. Adsorption isotherms have been obtained for thirty-three amino acids, vitamins and related substances using Darco G-60 as the adsorbent. The experimental data fit the equation commonly known as the Freundlich adsorption isotherm.

2. Several generalizations have been evolved from the data which show certain trends (based upon structure) in adsorption and in the $1/n$ values of the Freundlich equation. The presence and position of polar groups and the presence or absence of aromatic nuclei are important factors.

Austin, Texas Received March 23, 1942

[Contribution from the Research Laboratory of Armour and Company]

Studies on High Molecular Weight Aliphatic Amines and their Salts. VII. The Systems Octylamine–, Dodecylamine– and Octadecylamine–Water

By A. W. Ralston, Charles W. Hoerr and Everett J. Hoffman

Previous studies upon the behavior of aliphatic amines in water have been concerned only with amines of low molecular weight, and the literature pertaining to the higher homologs in water is confined to statements regarding their solubility. Preceding papers of this series have reported some aspects of the behavior of the hydrochlorides and acetates of primary aliphatic amines containing from 8 to 18 carbon atoms in the paraffin chain. This paper reports the behavior of octyl-, dodecyl- and octadecylamines in water. Since these three amines represent a cross-section of the series of normal primary aliphatic amines, a comparison of their water systems illustrates the effect of increased length of the alkyl chain upon such systems.

The applicability of the phase rule to colloidal systems has been demonstrated with respect to soap phases by McBain and his co-workers.[1] While they have shown that the phase rule can be applied in its usual form without the introduction of any new variable, they point out several of the assumptions and interpretations which must necessarily be made to fit the phase rule to some of the phenomena encountered in colloid chemistry. Of course, the original Gibbs deduction of the phase rule specifically excludes the effects of surface and boundary forces which are so important in connection with colloidal behavior; hence, in some cases certain observations must be omitted

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[1] McBain, Vold and Vold, This Journal, **60**, 1866 (1938).

or ignored. In other cases relative importances must be determined before an interpretation can be made. For example, no absolute meaning can be attached to the definitions of homogeneity and heterogeneity, since in dealing with colloids the degree of dispersion of the various phases has considerable bearing on their behavior.

Further complexities in the application of the phase rule to colloidal systems, aside from the confusion of the terminology, arise from the experimental difficulties encountered in dealing with these systems. The problem of establishing and maintaining equilibrium conditions is often an obstacle presented by the nature of the substances under observation. At certain temperatures the liquid phases may possess a very high viscosity, or the solid phases may exist in gelatinous or mesomorphic states. Hence, there is a problem of maintaining intimate admixture of the phases to bring about an equilibrium between them. In some cases, too rapid cooling may introduce a false phase which may not disappear for such a length of time that it would appear to be a true equilibrium phase. While these metastable phases have a given place in the phase diagram, they are misleading in the investigation of the stable phases. Thus it is essential, in studying a given phase, to demonstrate that equilibrium can be attained from higher and lower temperatures, and from higher and lower concentrations.

Procedure

Preparation of Materials.—Caprylonitrile, lauronitrile and stearonitrile were prepared by the action of ammonia upon the respective acids.[2] The caprylonitrile and lauronitrile (n^{25}_D 1.4184 and 1.4342, respectively) were purified by vacuum distillation,[3] and the stearonitrile (m. p. 42.0–43.0°) was crystallized from 95% ethanol. These nitriles were hydrogenated to the corresponding amines, which were then purified by fractional distillation *in vacuo*.[4] The amines used in this investigation had the following boiling points: octylamine, 46.5° (4 mm.); dodecylamine, 81.4° (1 mm.); and octadecylamine, 153.2° (1 mm.). Their freezing points, determined by the cooling curve method (*vide infra*), were −1.0, 28.0 and 52.5°, respectively. Titration with standard hydrochloric acid solution using methyl red as the indicator, in all cases yielded values exceeding 99.95% amine. These compounds were exposed to the atmosphere as little as possible in order to minimize absorption of carbon dioxide.

The water used in most of these experiments was distilled from an alkaline potassium permanganate solution in an all-Pyrex glass still, and was used in making up the amine samples directly after cooling without access to the air. Its specific conductance was 0.8×10^{-6} mho at 25°. The carbon dioxide content, therefore, was at a minimum. For the cooling curve measurements, boiled distilled water was used.

Experimental.—Five methods of investigation were followed. In every case, each amine–water sample prepared was first heated until it became a homogeneous liquid, or, in the ranges of concentrations where the systems do not become homogeneous at ordinary temperatures, until both components were liquefied and could be intimately mixed by shaking or stirring. This precaution has been stressed as a most desirable prerequisite in dealing with colloidal substances.[1]

The first experimental procedure was a synthetic method in which weighed amounts of the two components were sealed in glass tubes. After preliminary heating, the samples were suspended in a constant temperature water-bath and shaken regularly. The temperature of the bath was changed 0.1 to 0.2° about every half hour and the samples were observed visually to determine what phases were present. Since the various phases were arrived at both from higher and lower temperatures, and since the observed transition temperatures obtained in this manner could be duplicated within ±0.1°, it was considered that equilibrium had been attained.

The second method was an analytical procedure. Various compositions of amines and water (of approximately 50 g. total weight) were prepared in tightly stoppered flasks and, after preliminary heating, were placed in a constant temperature water-bath at several given temperatures. The flasks were shaken intermittently for two to three hours to allow the samples to attain equilibrium. Preliminary experimentation indicated that equilibrium was reached well within this time. After this interval, the separate phases were removed by means of a pipet and analyzed for amine content by titration with standard hydrochloric acid solution using methyl red as the indicator. The results obtained by this method showed that the analyses of samples existing in given phases at given temperatures gave calculated compositions of amine which agreed within 0.1% of those predicted by the synthetic method.

Cooling curves were run on amine–water mixtures in the following manner: an amine–water sample (10 g.), after being prepared in a tightly stoppered flask and heated to liquefaction, was transferred to a transparent Dewar flask (100 ml.) fitted with a rubber stopper through which were inserted a glass stirrer and a glass thermocouple well. This flask was swept with nitrogen before the introduction of the sample, and the stirrer was sealed at its insertion through the stopper with stopcock lubricant to minimize diffusion of carbon dioxide into the sample. Iron–constantan thermocouples were employed, and the reference junction was immersed in melting ice kept in a silvered Dewar flask (2 l.). Ice and water were used as the cooling bath for the amine–water samples above 0°, and acetone and solid carbon dioxide were used below this temperature. The thermal analyses thus obtained, for the most part, gave transition temperatures which agreed within ±0.1° of those obtained from the visual observations. However, in the cases in which samples containing the most highly hydrated forms of the two higher amines went through

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[2] Ralston, Harwood and Pool, THIS JOURNAL, **59**, 986 (1937).

[3] Ralston, Selby and Pool, *Ind. Eng. Chem.*, **33**, 682 (1941).

[4] Ralston, Selby, Pool and Potts, *ibid.*, **32**, 1093 (1940).

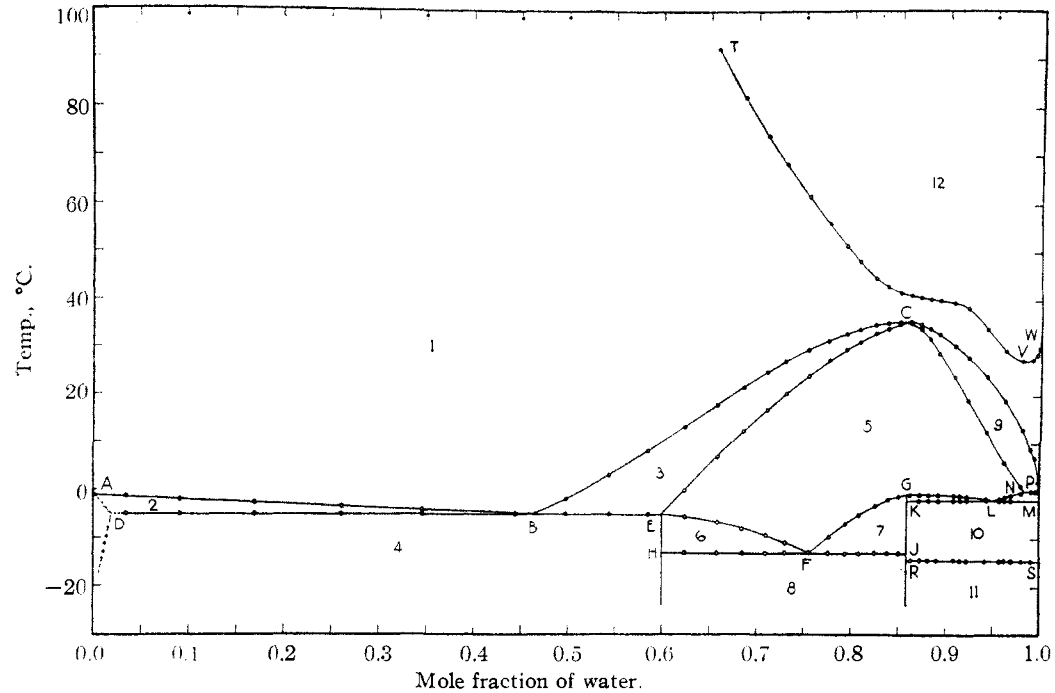


Fig. 1.—Transition temperatures of the system octylamine–water.

mesomorphic changes before crystallization, the cooling curves gave less accurate results because of the slower rate of heat transfer within the samples and the slow rate of formation of the crystalline phases.

Several of the transitions, chiefly the lowering of the freezing point of water by solution of the amines, were determined with a Beckmann thermometer in the usual manner. The transition temperatures obtained by this method agreed well within 0.1° of those obtained by the above procedures.

Finally, microscopic examinations with polarized light were made on a number of samples of varying composition in order to determine more definitely what phases were present. The samples were placed on ordinary glass slides and inclosed with thin glass cover slips sealed with paraffin. Observations were made chiefly at room temperature. However, some samples were heated gently over a small flame and were examined as they cooled. These observations verified the existence of the various phases in their given order as previously found by gross examination. Further observations of the order of appearance of certain phases were made by cooling the stage of the microscope below room temperature by means of a small piece of solid carbon dioxide.

Since transition temperatures could, in general, be duplicated to ±0.1°, and since the agreement of the results obtained by the various experimental procedures was also within ±0.1°, the transitions shown in the phase diagrams presented in this paper are probably accurate to ±0.2°.

Experimental Results

Octylamine–Water.—The temperature–composition relations of octylamine and water are shown graphically in Fig. 1. On this diagram, point A represents the freezing point of octylamine (−1.0°). Area 1 is isotropic solution. Two hydrates are formed, one having a composition of $(C_8H_{17}NH_2)_2 \cdot 3H_2O$ and the other $C_8H_{17}NH_2 \cdot 6H_2O$. The sesquihydrate exists as a crystalline solid below −5.0°, and above this temperature it breaks down to a mixture of hexahydrate and solution (area 3). The hexahydrate changes from a crystalline solid to a mesomorphic state at −14.5° (R). Between this temperature and −0.4° (G) it exists as a firm semi-solid of the smectic type of liquid crystal. From −0.4° (G) to its melting point, 34.6° (C), it exists as a nematic type of liquid crystal.

The portion of the diagram ABCED represents the equilibrium between octylamine and its hexahydrate. Octylamine precipitates from the isotropic solution (area 1) along AB and the hydrate precipitates along BC, giving a eutectic at B. Thus area 2 consists of a two-phase mixture of solid amine and solution, and area 3 of mesomorphic hydrate and solution. Below DBE (area 4) the system consists of a heterogeneous mixture of crystals. Microscopic examination of solutions at temperatures just below BC with polarized light shows the presence of inverted focal conics, indicating that the hydrate molecules are beginning to aggregate in liquid crystalline arrangements as the system cools below BC.

Examination of samples in area 5 shows a microscopically homogeneous fluid of a viscosity such that it will barely flow under its own weight at the lower temperatures, but of lower viscosity as the temperature is increased. Under polarized light, samples in this region reveal delicate thread-like lines of light, showing the presence of molecular layers in the liquid. The samples in this region can be considered to be one phase in accordance with the phase rule, analogous to the solid solutions of mixtures of metallic elements. In this case, however, instead of being a crystalline solid, the system consists of a highly dispersed mixture of amine and hydrated amine molecules in a mesomorphic state.

Octylamine sesquihydrate crystallizes from the isotropic solid solution (area 5) along EF while one of the forms of the hexahydrate precipitates out along FG, giving a eutectoid at F. Below HFJ (area 8) the system consists of a heterogeneous mixture of crystals.

The equilibria between the several forms of octylamine hexahydrate and water are in the concentration range of 0.857 to 1.0 mole fraction of water. The equilibrium between the nematic form of the hexahydrate and water is not shown clearly in the diagram. The eutectic between them (P) is located near 0.9996 mole fraction of water. Investigations in this neighborhood were considered relatively inaccurate since it was impossible to prevent contamination of such necessarily small amounts of amine with some carbon dioxide. However, measurement of the lowering of the freezing point of water along NP indicated that 0.0004 mole fraction of amine was in solution. The nematic octylamine hexahydrate precipitates from the isotropic solution (area 1) along CP, giving a two-phase mixture in area 9. On crossing CN, the microscopically homogeneous solid solution (area 5) is obtained.

On further cooling of the solid solution, smectic hexahydrate precipitates along GL, while water freezes along LN, giving a eutectoid at L. Thus below KLM (area 10) the system consists of a heterogeneous mixture of mesomorphic hydrate and ice. Since the crystalline hexahydrate forms at −14.5°, the system consists of a mixture of ice and hydrate crystals in area 11.

On being heated above TVW, the isotropic solution separates into two conjugate solutions, the layer of lower density being rich in amine, and the more dense one being water-rich. Analysis of the amine-rich layer by titration showed that the amount of octylamine at any given temperature was of the composition corresponding to that temperature on TV. The composition of the water-rich layer could not be determined accurately by analysis because small amounts of amine remained as a suspension of microscopic droplets in the water-rich layer.

Dodecylamine–Water.—The temperature–composition relations of dodecylamine and water are shown graphically in Fig. 2. On this diagram A represents the freezing point of dodecylamine (28.0°). Area 1 is isotropic solution. Three hydrates are formed, one having a composition of $(C_{12}H_{25}NH_2)_3 \cdot 2H_2O$, another $C_{12}H_{25}NH_2 \cdot 2H_2O$ and the third $C_{12}H_{25}NH_2 \cdot 4H_2O$. The lowest hydrate exists as a crystalline solid below 24.4° (F), while above this temperature it breaks down to a mixture of higher hydrate and solution. The dihydrate exists as crystalline solid below 15.4° (H), while between this temperature and 35.5° it exists as a smectic type of liquid crystal. At 35.5° the mesomorphic hydrate begins to liquefy, while at 36.5° (C) this mixture of hydrate and solution changes to isotropic solution. The dodecylamine tetrahydrate exists as crystalline solid below 14.0° (R), while above this temperature it exists as a smectic type of liquid crystal, changing to a form of the nematic type at 34.2° (P) and to another form of the latter type at 38.0° (O). At 48.0° (M) the tetrahydrate decomposes.

The equilibrium between dodecylamine and its dihydrate is similar to that between octylamine and its hexahydrate. Dodecylamine precipitates out of the isotropic solution (area 1) along AB, while the dihydrate freezes out along BC, giving a eutectic at B. Thus areas 2 and 3 consist of two phase mixtures, solid amine and solution, and solid dihydrate and solution, respectively. Below EBF (area 4) the system consists of a heterogeneous mixture of crystals of dodecylamine and its dihydrate.

Area 5 of this diagram is similar to area 5 of the octylamine–water system. Again the solid solution consists of a microscopically homogeneous mesomorphic mixture of amine and amine hydrate. As samples in this area are cooled, the lower hydrate precipitates out along FG and dihydrate freezes out along GH, giving a eutectoid at G. Below JGK (area 6) the system consists of a heterogeneous mixture of crystals of the two hydrates.

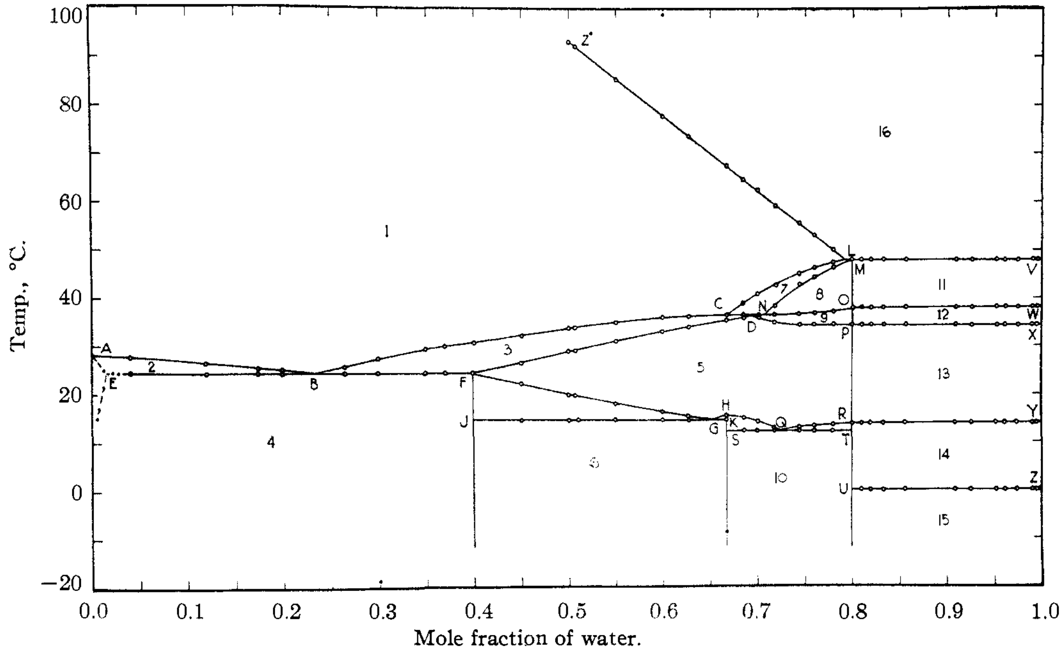


Fig. 2.—Transition temperatures of the system dodecylamine–water.

As the isotropic solution above CL is cooled, dodecylamine tetrahydrate freezes out, giving a two phase mixture of solid hydrate and solution in area 7. Below NM this mixture changes to a solid solution similar to that in area 5, while along NO the tetrahydrate transforms to another mesomorphic form giving a two phase mixture (area 9). On cooling this mixture, solid solution (area 5) is obtained.

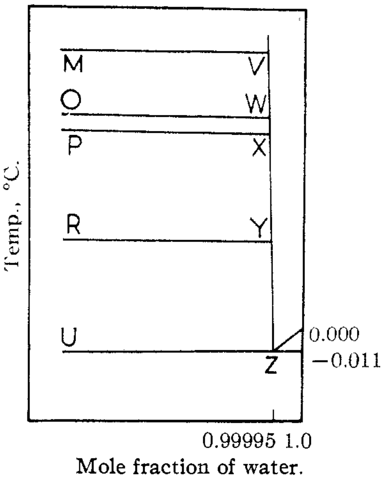


Fig. 3.—Diagram of eutectic between dodecylamine tetrahydrate and water (not drawn to scale).

Along HQ crystalline dodecylamine dihydrate freezes from the solid solution, while crystalline tetrahydrate appears along QR, giving a eutectoid at Q. Below SQT (area 10) the system consists of a mixture of these crystalline hydrates.

Beyond 0.8 mole fraction of water (MOPRTU), Fig. 2 shows the practically independent behavior of the various forms of dodecylamine tetrahydrate and of water. Measurements of the freezing point of water (along UZ) indicated that the eutectic between the tetrahydrate and water lies in the neighborhood of 0.99995 mole fraction of water. Hence, the isothermals (LMV, OW, PX, RY and UZ) intersect a curve (VWXYZ) representing the solubility of dodecylamine tetrahydrate in water. This region is illustrated by the enlarged diagram in Fig. 3. Thus, beyond 0.99995 mole fraction of water above Z to 0.0°, the system exists as isotropic solution.

In the part of the diagram between Z'LMOPRTU and VWXYZ in the temperature range investigated the system exists in all regions as two phases. In areas 11, 12 and 13 one of the phases is solution, and the other is the appropriate mesomorphic form of tetrahydrate (*vide supra*). In area 14 one of the phases is crystalline tetrahydrate, and the other is solution. In area 15 one phase is crystalline tetrahydrate, and the other is ice. Above LMV the system exists as two conjugate solutions similar to those occurring in the octylamine–water system (area 12, Fig. 1). The lines LMV, OW, PX and RY are isothermals. Their depression with increasing concentration is well within the experimental accuracy of their measurement.

The portion of the diagram in the neighborhood of area 12 is a region of formation of a fibrous, curd-like solid of hydrated amine. This is a metastable compound which is frequently obtained on cooling the two phase mixture of mesomorphic tetrahydrate and solution, and is never obtained on heating the system. It is not found in the octylamine– and octadecylamine–water systems. If samples in which this metastable product is obtained are held at room temperature, transformation to the smectic form of the tetrahydrate and solution takes place slowly. The metastable compound, in some cases, has remained for several months.

In Fig. 4 are shown photomicrographs of the crystalline forms of dodecylamine and of its three hydrates, together with the appearance of the metastable curd-like compound.

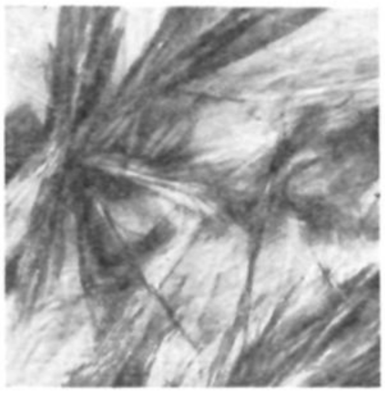
Octadecylamine–Water.—The temperature–composition relations of octadecylamine and water are shown graphically in Fig. 5. On this diagram A represents the freezing point of octadecylamine (52.5°). Area 1 is isotropic solution. Two hydrates are formed, one having a composition $(C_{18}H_{37}NH_2)_3 \cdot H_2O$, and the other $C_{18}H_{37}NH_2 \cdot 2H_2O$. The lower hydrate exists as crystalline solid below 50.5°, while above this temperature it breaks down to a mixture of dihydrate and solution. The dihydrate exists as crystalline solid below 43.3°, while above this temperature it transforms to a smectic state. At 64.0° the dihydrate decomposes.

In Fig. 5 octadecylamine crystallizes from the isotropic solution (area 1) along AB, while the dihydrate precipitates along BC, giving a eutectic at B. Thus areas 2 and 3 consist of two-phase mixtures of solid amine and solid dihydrate, respectively, and solution. Below EBF (area 4) the system consists of a heterogeneous mixture of crystals.

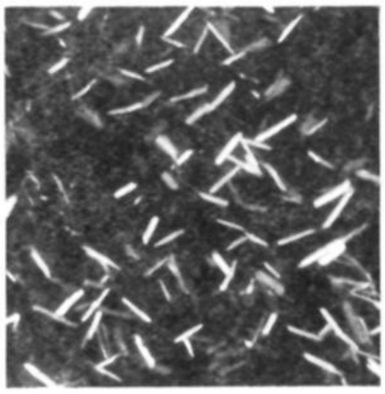
Samples in area 5 are solid solutions microscopically indistinguishable from the corresponding phase of the other amines (area 5, Figs. 1 and 2). On cooling this solid solution, the lower octadecylamine hydrate freezes out along FG and the dihydrate along GH, giving a eutectoid at G. Below JGK (area 6) the system consists of a mixture of the two crystalline hydrates.

The part of the diagram beyond 0.667 mole fraction of water (DHKL) represents the behavior of the several forms of the dihydrate with water. As in the case of dodecylamine tetrahydrate, there is a eutectic between the octadecylamine dihydrate and water similar to that shown in Fig. 3. As far as was determined, the solubility of this dihydrate in water must be less than 1.8×10^{-6} g./liter, since this amount must be in solution to lower the freezing point of water 0.001°. However, no such depression was observed by measurement with a Beckmann thermometer. Hence, the eutectic in this case is beyond 0.999991 mole fraction of water. No further attempt was made to determine more accurately the location of the solubility curve through MNP in Fig. 5.

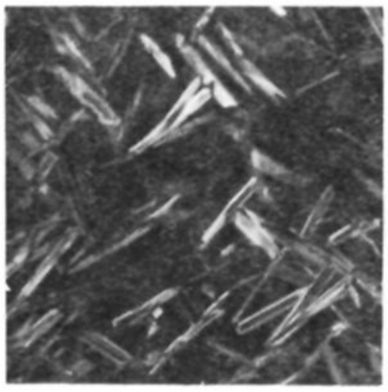
Between DHKL and MNP the octadecyla-



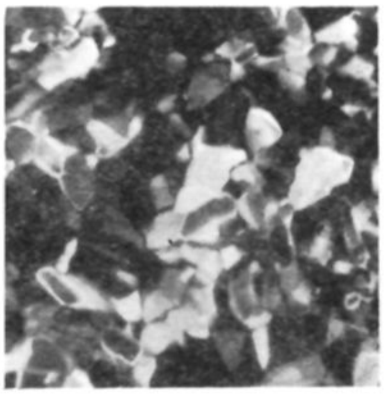
(a) $C_{12}H_{25}NH_2$.



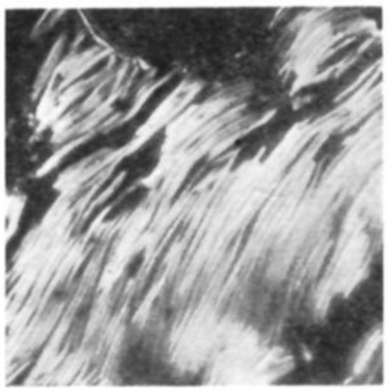
(b) $(C_{12}H_{25}NH_2)_3 \cdot 2H_2O$.



(c) $C_{12}H_{25}NH_2 \cdot 2H_2O$.



(d) $C_{12}H_{25}NH_2 \cdot 4H_2O$.



(e) $C_{12}H_{25}NH_2 \cdot xH_2O$.

Fig. 4.—Crystalline forms of dodecylamine and its hydrates, with polarized light at ×200.

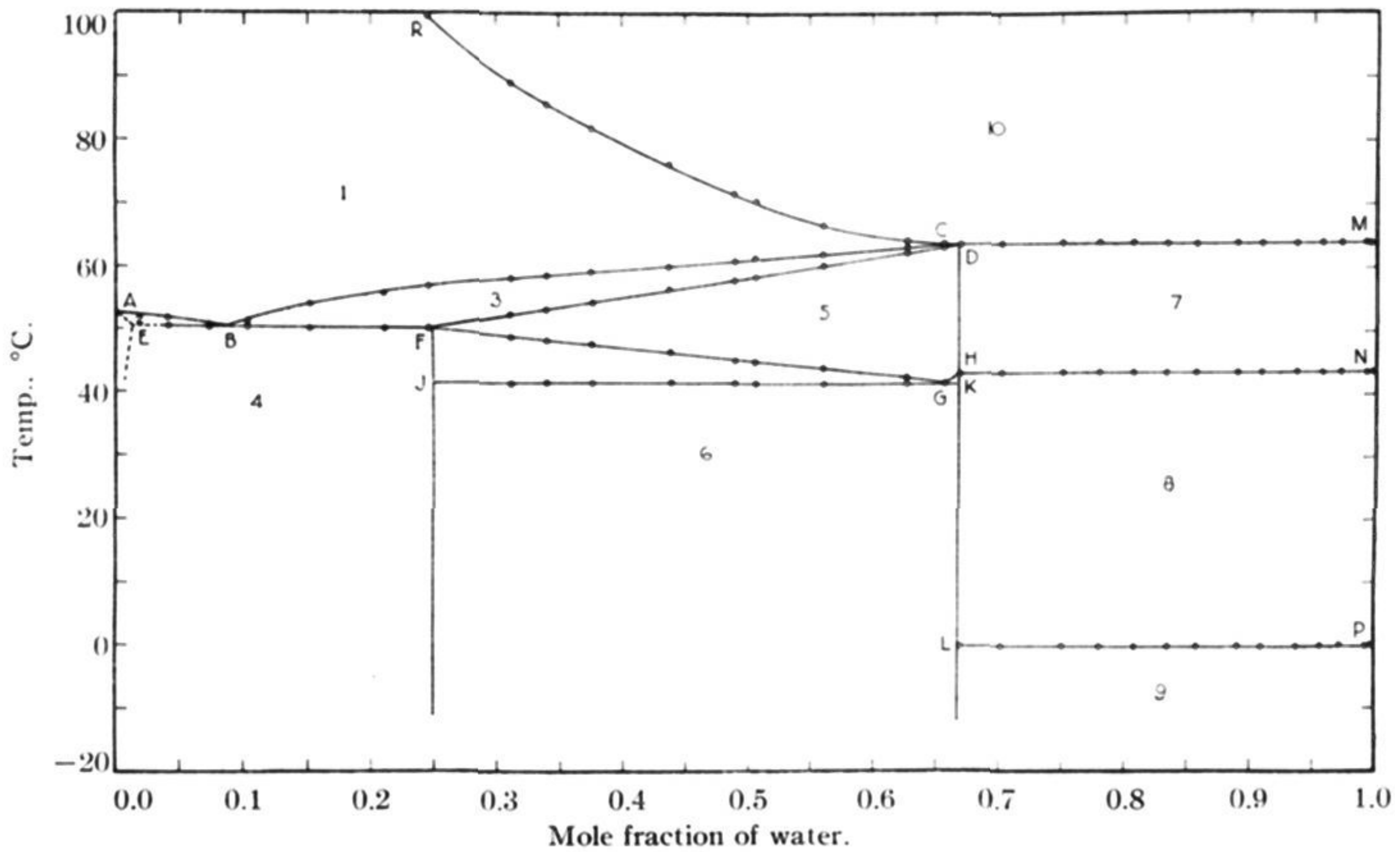
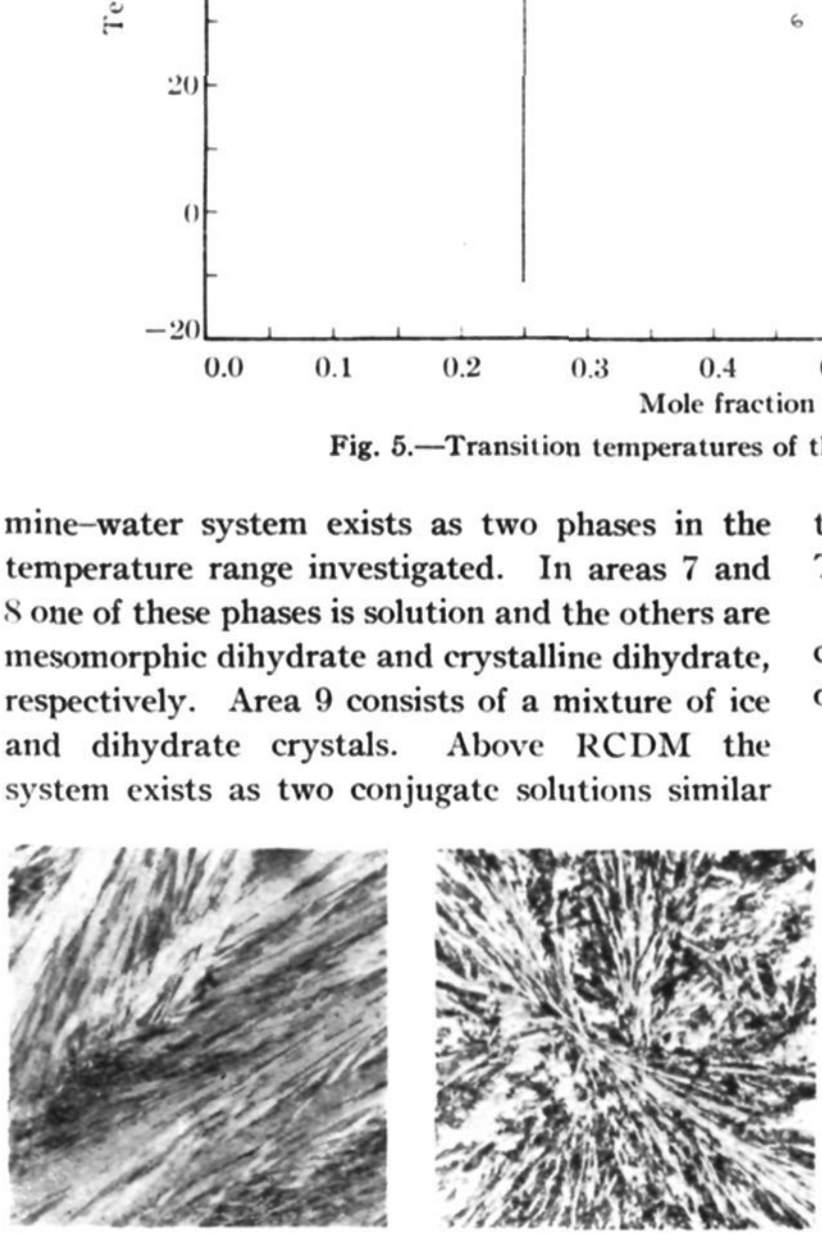


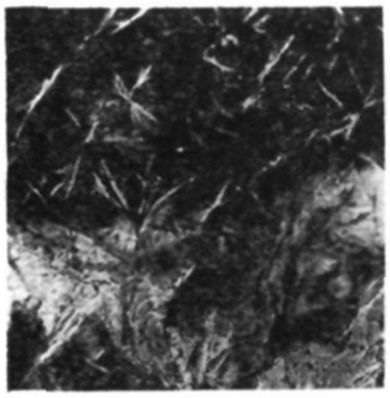
Fig. 5.—Transition temperatures of the system octadecylamine-water.

mine–water system exists as two phases in the temperature range investigated. In areas 7 and 8 one of these phases is solution and the others are mesomorphic dihydrate and crystalline dihydrate, respectively. Area 9 consists of a mixture of ice and dihydrate crystals. Above RCDM the system exists as two conjugate solutions similar to those in the other two systems investigated. The lines DM and HN are isothermals.

In Fig. 6 are shown photomicrographs of the crystalline forms of octadecylamine and its hydrates.



(a) $C_{18}H_{37}NH_2$. (b) $(C_{18}H_{37}NH_2)_3 \cdot H_2O$.



(c) $C_{18}H_{37}NH_2 \cdot 2H_2O$.

Fig. 6.—Crystalline forms of octadecylamine and its hydrate, with polarized light at ×200.

Discussion

Qualitatively the three systems investigated are similar. All three amines form hydrates; the higher the molecular weight, the lower the degree of hydration. Microscopic examinations indicated that hydrates of the lower amines tend to form more nearly perfect crystals than hydrates of the higher amines. As would be expected, the lower amines and their hydrates are considerably more soluble in water than the higher homologs. Of the systems investigated, that of octylamine–water is the only one in which there is an isotropic liquid region across the whole range of concentrations.

The amine hydrates found, with the exception of the lowest hydrate of each amine, pass through one or more mesomorphic states before their melting or decomposition points are reached. The hydrates of the lower members of the series tend toward the nematic type of liquid crystal, while those of the higher members tend toward the smectic type.

In the case of octylamine, the hexahydrate is relatively unstable, the water of hydration being very loosely bound to the amine molecules.

This is shown by the relative flattening of the curve as the melting point of the hydrate is approached from higher and lower concentrations, indicating that considerable change in the water content of the hydrate is necessary to change the melting point to any great extent. Since the addition of an impurity (in this case one of the decomposition products) tends to cause lowering of the melting point of a given compound, and since the lowering is greater with greater compound stability, the relative instability of this hydrate is indicated. The decomposition of the other amine hydrates is evidence of their instability.

The fibrous, curd-like, metastable compound formed only in the dodecylamine system suggests the behavior of dodecylamine hydrochloride in water.[5] In the latter system, also, a similar fibrous, curd-like, metastable compound was found on rapid cooling of systems containing large amounts of water. This behavior is not observed in the case of the octadecylamine hydrochloride–water system, and likewise it is absent in the present case of octadecylamine–water.

In each of the three diagrams presented the dotted lines at the left of the figures show the existence of a small region of solid solution of amine and amine hydrate. While these areas were indicated, their exact location was not verified by direct measurement.

With the interpretations and limitations which have been placed upon the mesomorphic states, and since equilibrium conditions have been evidenced by the agreement of the transition temperatures obtained by several different experimental methods, the applicability of the phase rule to these colloidal systems has been demonstrated. The equilibria between the amines and their respective hydrates are similar to phase diagrams for ordinary crystalloidal compounds. In the case of the higher amine hydrates, their insolubility and their mesomorphic changes account for the numerous isothermals which are present in their diagrams.

The authors are indebted to Drs. J. A. Wilkinson and H. A. Wilhelm of Iowa State College for their assistance and helpful suggestions during the course of this investigation.

Summary

1. The systems octylamine–water, dodecylamine–water and octadecylamine–water have been investigated.

2. The phase rule has been applied to these systems.

3. The following hydrates have been found: $(C_8H_{17}NH_2)_2\cdot 3H_2O$ (dec. $-5.0°$); $C_8H_{17}NH_2\cdot 6H_2O$ (m. p. 35.6°); $(C_{12}H_{25}NH_2)_3\cdot 2H_2O$ (dec. 24.4°); $C_{12}H_{25}NH_2\cdot 2H_2O$ (m. p. 36.5°); $C_{12}H_{25}NH_2\cdot 4H_2O$ (dec. 48.0°); $(C_{18}H_{37}NH_2)_3\cdot H_2O$ (dec. 50.5°); and $C_{18}H_{37}NH_2\cdot 2H_2O$ (dec. 64.0°).

CHICAGO, ILLINOIS RECEIVED JANUARY 12, 1942

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[5] Ralston, Hoffman, Hoerr and Selby, THIS JOURNAL, **63**, 1598 (1941).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

Plumbic Acetate–Anhydrous Acetic Acid Solutions

BY ARTHUR W. DAVIDSON, W. CLARENCE LANNING AND SR. M. MAXINE ZELLER

It is well known that whenever a comparison is made between two hydroxides of the same metal, the one in which the metal is in the lower state of oxidation is the more basic and the more soluble in water. A partial qualitative explanation of this fact may be based upon the distribution of electrons about the metal atom.[1] Evidence of an analogous relationship in non-aqueous systems has hitherto been limited to observations on the solubilities of sulfates in sulfuric acid.[2]

The fact that plumbic acetate (lead tetraacetate), unlike most plumbic salts, is stable at ordinary temperatures and may, in fact, be prepared rather readily, affords an opportunity for a comparison of the solubilities of the two acetates of lead in anhydrous acetic acid, solutions of plumbous acetate in this medium having already been studied.[3] Hutchinson and Pollard,[4] who were the first to make an extensive study of the properties of plumbic acetate, reported that it is

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[1] See, for example, O. K. Rice, "Electronic Structure and Chemical Binding," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, pp. 428–9.

[2] Kendall and Davidson, THIS JOURNAL, **43**, 979 (1921).

[3] (a) Davidson and McAllister, *ibid.*, **52**, 507 (1930); (b) Davidson and Chappell, *ibid.*, **55**, 4524 (1933).

[4] Hutchinson and Pollard, (a) *J. Chem. Soc.*, **63**, 1136 (1893); (b) *ibid.*, **69**, 212 (1896).