Studies on High Molecular Weight Aliphatic Amines and their Salts.   I.   Behavior of the Hydrochlorides of Dodecylamine and Octadecylamine in Water

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With few exceptions, the studies of the behavior of high molecular weight aliphatic compounds in water have dealt with those compounds in which the aliphatic group is in the anionic portion of the molecule.   The present study on amine salts deals with compounds in which the aliphatic group is in the cationic portion of the molecule.

Investigations by Krafft and Strutz[1] and by Krafft[2] indicated that aqueous solutions of hexadecylamine hydrochloride possessed certain properties of soap solutions: e. g., formation of a stable foam over a wide range of concentration, formation of an extremely viscous mass at high concentrations, and an elevation of the boiling point much less than that predicted if the solute existed as a simple molecule or were completely dissociated.   On this basis, they postulated the existence of high molecular weight agglomerates or colloidal particles of hexadecylamine hydrochloride.

The behavior of anionic colloidal electrolytes in water is well known.   The data herewith presented indicate that, as regards phase rule considerations, the behavior of the high molecular weight aliphatic amine salts in water is analogous to that of anionic colloidal electrolytes.

Experimental Part

Preparation of Materials.—Dodecylamine and octadecylamine were prepared by the conversion of lauric and stearic acids,[3] respectively, to nitriles[4] and hydrogenation of the nitriles to amines.   The lauronitrile was purified by fractional distillation (n^{25}D 1.4338–1.4344), and the stearonitrile was purified by crystallization from ethanol (m. p. 42.0–43.0°).   After hydrogenation the amines were purified by fractional distillation in vacuo to separate them from any unchanged nitrile or secondary amine.[5]   The amines thus purified were converted into the corresponding hydrochlorides.   These salts were then crystallized from appropriate solvents (as indicated below) to remove any unchanged amine.

Dodecylamine Hydrochloride.—Dodecylamine (150 g.) was dissolved in ethanol (485 ml.) in a one-liter balloon

flask, and hydrochloric acid (concd., 97.5 ml.) was added dropwise to the solution while it was mechanically stirred.   The ethanol was removed by distillation until foaming became too great.   Successive portions of benzene were then added and removed by distillation of the ternary mixture ethanol–water–benzene until no water remained.   Foaming ceased when water was no longer present.   The residue was then air dried.   The dry residue was crystallized as follows: a portion of the crude dodecylamine hydrochloride (30 g.) was dissolved in warm ethanol (90 ml.), and diethyl ether (U. S. P., 500 ml.) was added.   The dodecylamine hydrochloride was allowed to crystallize at room temperature, and it was then cooled to 5° to complete the process.   The dodecylamine hydrochloride was recrystallized twice, and it was then air dried.   It decomposed on heating before a melting point was reached.

Octadecylamine Hydrochloride.—Octadecylamine (8 g.) was dissolved in ethanol (25 ml.) in a 500-ml. balloon flask, and hydrochloric acid (concd., 5.0 ml.) was added dropwise.   The ethanol, water and excess hydrogen chloride were removed by heating the mixture on a steam-bath under reduced pressure (15 mm.).   Foaming occurred until the product was dry.   The residue was dissolved in ethanol (155 ml.), and diethyl ether (U. S. P., 350 ml.) was added.   The mixture was refluxed, and the amine salt was then allowed to crystallize.   The product was recrystallized from ethanol (200 ml.) and diethyl ether (500 ml.).   The octadecylamine hydrochloride was air dried; it decomposed on heating before a melting point was reached.

Water.—Distilled water was boiled to remove dissolved gases prior to its use in the preparation of samples for the solubility studies.

Procedure.—The method employed for the determination of the solubility of the amine salts in water was similar to that devised by Alexejew[6] for the study of binary liquid systems.   This is a synthetic method in which weighed amounts of the two components are sealed in glass tubes which are then rotated in a heating bath while the temperature is increased slowly.   The rate of heating was approximately five degrees per hour except at the temperature ranges in which it had been determined in preliminary runs that phase changes occurred.   In these ranges the rate of heating was reduced to one-half degree or less per hour.   Observations made in this manner were found to be reproducible to one-tenth of a degree.

Water was used in the heating bath below 95° and above this temperature a clear mineral oil.   The temperature at which the contents of a tube became clear and homogeneous was regarded as the solution temperature for that particular composition.   Visual observations of other changes that occurred at various temperatures were also recorded.   To determine more definitely what phases were present some samples were examined by means of a polarizing microscope.

(1) Krafft and Strutz, Ber., **29**, 1328 (1896).

(2) Krafft, ibid., **32**, 1596 (1899).

(3) The lauric and stearic acids used were the commercial products Neo-Fat 11 and Neo-Fat 1–65, respectively, marketed by Armour and Company.   The stearic acid was crystallized three times from acetone before it was converted to the nitrile (m. p. 69–70°).

(4) Ralston, Harwood and Pool, This Journal, **59**, 986 (1937).

(5) Ralston, Selby, Pool and Potts, Ind. Eng. Chem., **32**, 1093 (1940).

(6) Alexejew, Wied. Ann., **28**, 305 (1886).

All samples were heated until they were fluid and well mixed before any observations were made.

Cooling curves were run for some compositions to check transition temperatures.

Experimental Results

Dodecylamine Hydrochloride.—In the ensuing description of the behavior of this system, the results obtained when a given sample was maintained at a low temperature (*ca.* 0°) for several hours and was then heated slowly will be referred to as those applying to the stable system. The results obtained when a sample was chilled rapidly and was then heated rapidly or placed immediately in a water-bath at some temperature selected by trial methods will be referred to as those applying to the metastable system.

The transition temperatures for the system dodecylamine hydrochloride–water are shown graphically in Fig. 1. In Table I are listed the composition (weight per cent.) and the temperatures at which liquefaction was first visually observable for several of the samples of dodecylamine hydrochloride investigated. These values are not included in Fig. 1.

TABLE I

LIQUEFACTION TEMPERATURES IN THE $C_{12}H_{25}NH_2 \cdot HCl$–$H_2O$ SYSTEM

Per cent. $C_{12}H_{25}NH_2 \cdot HCl$ by wt.	Metastable system	Stable system	Per cent. $C_{12}H_{25}NH_2 \cdot HCl$ by wt.	Metastable system	Stable system
0.8464	0.5	0.5	23.62	21.0	29.0
1.368	1.0	1.0	28.27	..	29.5
2.602	5.0	5.0	29.93	22.0	..
3.483	7.5	11.0	31.14	..	30.5
4.652	13.0	17.7	34.33	22.0	
6.082	..	20.5	39.14	22.4	
6.461	15.8	..	42.50	22.8	
10.12	17.5	26.0	45.52	23.0	
12.46	18.2	..	49.86	23.0	
15.69	19.0	27.6	55.17	23.0	
18.29	20.0	28.0	60.54	23.0	
21.53	20.5	28.5			

Stable System.—In Fig. 1 all curves and areas refer to the stable system with the exception of curve AB which refers to the metastable system. Area I consists of non-viscous, isotropic liquid. Area II represents a thixotropic gel. The boundaries of this region were determined when agitation was merely sufficient to maintain constant temperature. Examination with a polarizing microscope of samples in area III indicates that they are in the mesomorphic state. This system breaks down along the boundary of area IV to give a heterogeneous mixture of two liquids which

coalesce to form the isotropic liquid of area I on further heating. Microscopic examination of samples in area V reveals the presence of monoclinic prisms and solution. The solution is held within the crystal mass so that its presence is not observed by visual examination of the samples in the tubes.
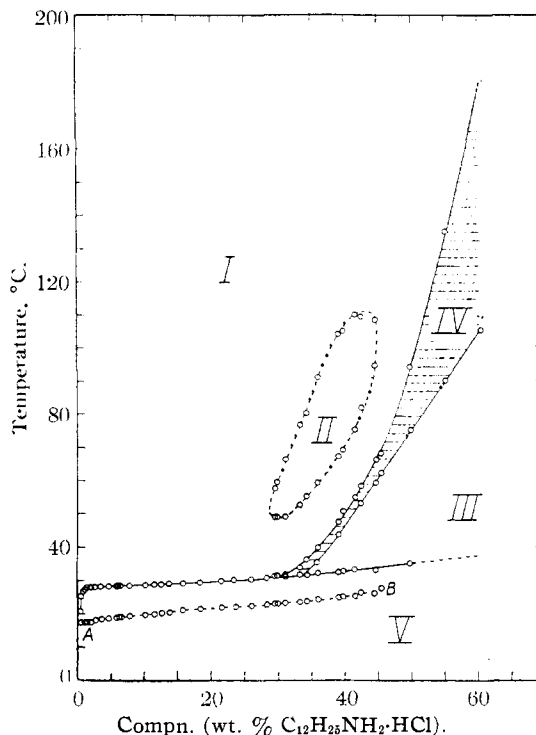

Fig. 1.—Transition temperatures for the system $C_{12}H_{25}$-$NH_2 \cdot HCl$–H_2O.

Metastable System.—In Fig. 1 the curve AB refers to the metastable system. In order to obtain these values, the following experimental procedure was adopted. A sample was warmed until it was liquid and homogeneous (area I); it was then plunged into a salt–ice-bath until it was frozen, and finally it was placed in a water-bath at such a temperature that it would liquefy and clear (curve AB) without further heating. In order to obtain curve AB it was necessary to repeat this operation several times using water-baths that differed from each other in temperature by only one-tenth or two-tenths of a degree. The water-bath temperature chosen for the first trial was based on observations made when the samples were heated rapidly. If a sample was maintained for a few minutes after clearing at a temperature represented by a point on curve AB, white solid would again form, and the behavior of the stable

system would be observed on further heating. The white solid obtained in this case had a stringy, curd-like appearance, and, on standing, liquid (either water or solution) separated from it. No liquid separated from the solid obtained along the stable curve.

Cooling curves run on samples containing less than 30% dodecylamine hydrochloride indicated that there was neither a thermal effect nor crystal formation until the curve AB was reached. However, if the temperature was maintained slightly below the solubility curve of the stable modification (*ca.* 26°), and a crystal of dodecylamine hydrochloride was added, crystal formation proceeded to completion without change of temperature. If the sample was warmed after precipitation along curve AB, complete solution was not attained until the solubility curve of the stable form was reached.

Since decomposition began in the range 140–150°, samples containing more than approximately 60% dodecylamine hydrochloride were not investigated.

Octadecylamine Hydrochloride.—The transition temperatures for the system octadecylamine hydrochloride–water are shown graphically in Fig. 2. A comparison of Fig. 2 with Fig. 1 indi-
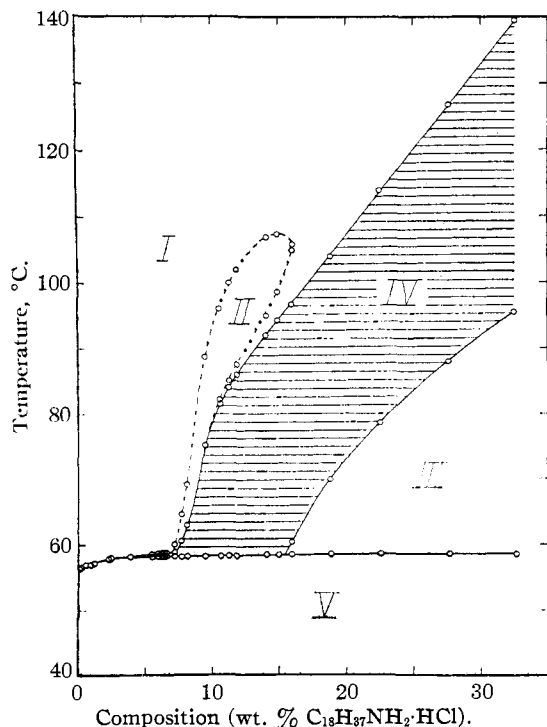

Fig. 2.—Transition temperatures for the system $C_{18}H_{37}$-$NH_2 \cdot HCl$–H_2O.

cates that there is a marked similarity between the two systems except that a metastable modification was not observed in the case of octadecylamine hydrochloride. This was confirmed by cooling curve data. Area I represents an isotropic liquid, and area II is a thixotropic gel. Area III represents the mesomorphic state which breaks down along the boundary of area IV to give a two phase system on further heating. This two phase system is so viscous that it does not flow. Clearing occurs along the boundary between areas IV and I. Samples containing less than approximately 16% octadecylamine hydrochloride do not pass through the mesomorphic state, and those containing between approximately 4% and 16% octadecylamine hydrochloride change directly from area V (crystals plus trapped solution) to the two phase system of area IV along an isothermal boundary.

Thermal decomposition precluded the investigation of samples containing more than approximately 32% octadecylamine hydrochloride.

Discussion

All of the solutions investigated, except those that were extremely dilute, produced foams that were stable for several hours. There are several other definite indications of colloidal properties in these systems; *e. g.*, the thixotropic behavior in certain concentrations, the long time required to attain equilibrium conditions, the presence of stringy, curd-like fibers noted in many of the samples and the difference between their solubility (or at least their rate of solution) and that of other solid forms produced in the same sample under different conditions, and the very high temperature coefficient of solubility over a wide concentration range.

The failure of extremely dilute solutions to foam and the electrical conductance of these solutions (based on unpublished, preliminary work in this Laboratory) indicate that at low concentrations we are dealing with completely dissociated electrolytes. However, colloidal properties are manifest at a relatively low concentration.

The phase rule diagrams resemble those obtained for compounds in which the aliphatic group is in the anionic portion of the molecule.

Summary

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

2. Observations indicate a strong similarity between the anionic and cationic high mo-lecular weight aliphatic compounds in water.

CHICAGO, ILLINOIS

Surface Conditions of Precipitates and Rate of Reaction. IV. Reduction of Mercurous Chloride by Hydroxylamine

BY T. H. JAMES

Gurney and Mott[1,2] have proposed the following mechanism for the reduction of silver halides by developing agents[2]: "The molecules of the developer hand over electrons to the metallic silver speck, and raise its potential relative to that of the halide grain. The interstitial silver ions which are present in the halide are then attracted to the silver speck; they will move up to it and adhere to it. Of course, as fast as the silver ions in the grain are used up, new ones are formed. The halogen escapes from the surface of the crystal, and not from the metal–compound interface. Interstitial ions, which may have come from quite distant parts of the crystal, flow through the crystal and join the metal at the interface." A property of silver halide which is essential for the Gurney–Mott theory is that of electric conductivity by ionic migration. The silver halides are known to exhibit relatively large conductivity even at room temperature. Tubandt[3] and coworkers have shown that the conductivity of the silver halides is due principally to the movement of silver ions. Hence, this requirement is fulfilled for the silver halides.

The mercurous halides present an entirely different situation. They are much more molecular in structure than the silver halides, and may be considered to be built up of an aggregation of XHgHgX "molecules," so distributed that each Hg atom is surrounded by four X atoms of other molecules, and vice versa.[4] Ketzer[5] reported that the specific conductivity of well-dried mercurous chloride is not greater than 10^{-11} ohm^{-1}, which was about the limit of sensitivity of the apparatus he employed. This is to be compared with a conductivity of about 10^{-8} ohm^{-1} for the silver halides.[6] It does not appear possible that interstitial mercurous ions (Hg_2^{++}) could form in or travel through the mercurous chloride crystal. It is, therefore, of interest to compare the reduction of this material by the developing agent, hydroxylamine, with that of silver chloride.[7] The experimental results which follow demonstrate that the two processes are formally quite similar.

Experimental

The general procedure employed in this investigation was the same as that used previously with silver chloride.[7] A stock solution of mercurous nitrate was prepared by dissolving 2.5 mmoles of $Hg_2(NO_3)_2$ in 20 ml. of 1.00 M nitric acid. This solution was stored in the dark over mercury. No kinetically detectable change occurred within a week, the maximum period any one stock solution was kept. Solutions not stored over mercury showed significant change, due to a poisoning action of the mercuric salts formed.

Mercurous chloride was precipitated by addition from a pipet of 5.0 ml. of 0.20 M sodium chloride to 2.0 ml. of stock mercurous nitrate diluted to 15 ml. with water. Thus, an excess of 0.5 mmole of Cl$^-$ was present in the standard precipitation. The mercurous solution was mechanically stirred during the addition of sodium chloride solution, and the tip of the pipet was kept below the liquid surface. Reduction was carried out at 20.00 ± 0.03° in the presence of phosphate buffer.

Reduction of Mercurous Nitrate by Hydroxylamine.— Some preliminary experiments were made on the reduction of mercurous nitrate at pH 3.9, using an acetate buffer. The tendency of mercurous nitrate to hydrolyze at this pH, together with the poor stability of colloidal mercury, limited the extent to which quantitative experiments could be carried out in this case. However, the reaction curve was definitely auto-accelerating in form, and the reduction was markedly catalyzed by added colloidal mercury or colloidal silver. Silver nitrate in amounts equivalent to the silver sol used had no noticeable effect upon the reaction rate.

Mercuric chloride is reduced only very slowly if at all by

(1) R. W. Gurney and N. F. Mott, Proc. Roy. Soc., (A)164, 151 (1938).

(2) N. F. Mott, Reports on Progress in Physics, 6, 186 (1939); N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," The Clarendon Press, Oxford, 1940.

(3) C. Tubandt, "Handbuch der Exper. Physik," Vol. XII, Part I, p. 384 ff., Leipzig, 1932; C. Tubandt and S. Eggert, Z. anorg. allgem. Chem., 110, 196 (1920).

(4) R. J. Havighurst, Am. J. Science, 10, 15 (1925); Ch. Mauguin, Compt. rend., 178, 1913 (1924); M. L. Huggins and P. L. Magill, THIS JOURNAL, 49, 2357 (1927).

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(6) W. Lehfeldt, Z. Physik, 85, 717 (1933).

(7) T. H. James, THIS JOURNAL, 62, 536, 1649 (1940).