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Studies on High Molecular Weight Aliphatic Amines and Their Salts. XI. Transference Numbers of Some Primary Amine Hydrochlorides in Aqueous Solution and Their Significance in the Interpretation of the Micelle Theory*

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The micelle theory[1] was devised to explain the anomalous behavior of colloidal electrolytes in water. While the theory has been substantially modified since its introduction, its basis is, essentially, the assumption of the existence of two species of micelles. Several alternate theories have been proposed, chief among them being Hartley's suggestion,[2] supported by considerable experimental proof, that only one type of micelle exists. The contention[3] that soap solutions consist only of the dissociated salts of fatty acids rather than as colloidal micelles has been shown to be untenable,[4] and the postulation of a paraffin chain network[5] has been proved invalid.[6,7]

The chief differences between the several interpretations of the micelle theory have been due to incomplete experimental data concerning the nature of the colloidal micelles, and of the concentrations at which they occur. Numerous studies by means of a wide variety of experimental procedures, such as conductance, transference number, diffusion, sedimentation, density, osmotic activity, viscosity and solubility measurements, have been reported in support of each of the theories. However, in recent years, a number of X-ray absorption investigations have been reported,[8–15] which, while there are minor variations in detail, are in good agreement that two definite forms of micelle exist in solutions of colloidal electrolytes. Thus, one of the major objections to the micelle theory has been refuted. Further X-ray investigations may establish definitely the ranges of concentration over which these micelles occur.

This paper presents the transference numbers in water at 60° of the amine hydrochlorides containing 8, 10, 12, 14, 16 and 18 carbon atoms in the paraffin chain, with transference numbers of dodecylamine hydrochloride at several other temperatures. The ionic conductances of these salts have been calculated from their previously reported equivalent conductances.[16,17] Their degree of hydrolysis at several concentrations has been measured and compared with the *p*H values which were calculated from the ionization constants of the amines.[18] With these experimental data, and the measurements of solubility,[19,20] surface tension,[21] and viscosity,[17] this paper attempts to explain the behavior of the amine hydrochlorides in water in terms of the recent developments of the micelle theory.

Experimental

Materials.—The amine salts employed in the transference experiments were those used in the previous conductance studies.[16,17] Their preparation and some of their constants have been reported elsewhere.[19,22] The amine salt solutions were prepared by weight in previously steamed, glass-stoppered flasks with freshly distilled conductivity water whose specific conductance at no time exceeded 1.2×10^{-6} mhos at 60°.

Apparatus.—Two transference cells were used in the course of this investigation. The first was of the type used by Carrara.[23] It was constructed of Pyrex tubing and consisted of two electrode chambers (1.4 cm. diam. × 18.5 cm.) each with a bulb (2.8 cm. diam.) blown in the lower part, and a stopcock at the lower end. The chambers were connected near their upper ends by a U-tube which had a separate stopcock to allow rapid drainage of this central portion of the cell. The total volume of the cell was

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(1) McBain, *Trans. Faraday Soc.*, **9**, 99 (1913); *Kolloid-Z.*, **13**, 56 (1913); *J. Chem. Soc.*, **105**, 417, 957 (1914); Reychler, *Kolloid-Z.*, **13**, 252 (1913); *Bull. soc. chim belg.*, **27**, 217 (1913); *Z. Chem. Ind. Kolloide*, **12**, 277 (1913); McBain and Salmon, THIS JOURNAL, **42**, 426 (1920).

(2) Hartley, "Aqueous Solutions of Paraffin Chain Salts," Hermann et Cie, Paris, 1936.

(3) Linderström-Lang, *Compt. rend. trav. lab. Carlsberg*, **16**, 47 pp. (1926).

(4) McBain, THIS JOURNAL, **50**, 1636 (1928).

(5) Howell and Warne, *Proc. Roy. Soc.* (London), **A160**, 440 (1937)

(6) Hartley, *Trans. Faraday Soc.*, **34**, 1283 (1938); *Kolloid-Z.*, **88**, 22 (1939).

(7) McBain, Dye and Johnston, THIS JOURNAL, **61**, 3210 (1939).

(8) Thiessen and Spychalski, *Z. physik. Chem.*, **156A**, 435 (1931).

(9) Hess and Gundermann, *Ber.*, **70B**, 1800 (1937).

(10) Hess, Philippoff and Kiessig, *Kolloid-Z.*, **88**, 40 (1939).

(11) Stauff, *ibid.*, **89**, 224 (1939); **96**, 244 (1941); *Naturwissenschaften*, **27**, 213 (1939).

(12) Kiessig and Philippoff, *ibid.*, **27**, 593 (1939).

(13) Kiessig, *Kolloid-Z.*, **96**, 252 (1941); **98**, 213 (1942).

(14) Philippoff, *ibid.*, **96**, 255 (1941).

(15) Ross, *J. Phys. Chem.*, **46**, 414 (1942).

(16) Ralston, Hoerr and Hoffman, THIS JOURNAL, **64**, 97 (1942).

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

(18) Hoerr, McCorkle and Ralston, *ibid.*, **65**, 328 (1943).

(19) Ralston, Hoffman, Hoerr and Selby, *ibid.*, **63**, 1598 (1941).

(20) Hoerr and Ralston, *ibid.*, **64**, 2824 (1942).

(21) Hoffman, Boyd and Ralston, *ibid.*, **64**, 498 (1942).

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

(23) Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., Inc., New York, 1932, Vol. I, p. 681, Fig. 14H.

approximately 75 ml., each electrode chamber containing about 29 ml. The anode consisted of a disk (1.2 cm. diam. × 0.2 cm.) of cadmium fastened to a platinum wire which was fused through a soft glass tube of such length that the electrode was located at the center of the bulb of the chamber. The cathode consisted of a coil (0.6 cm. diam. × 1.5 cm.) of platinum wire sealed through a soft glass tube, the whole electrode being encased in a tubular glass sheath (1.0 cm. diam.) which extended to the bottom of the cathode chamber and was open to the solution at its lower end. The electrodes were connected to the circuit by mercury contacts.

In order to obtain greater experimental accuracy, and to overcome some of the disadvantages of this smaller cell, a second cell was procured. This cell was a duplicate of that used by Washburn.[24] It was constructed of 25-mm. Pyrex tubing with stopcocks of the same bore as the inside diameter of the tubing. The average distance through the cell from anode to cathode was about 100 cm., and the total volume of the cell was approximately 325 ml. The anode consisted of a coil (1.8 cm. diam. × 5 cm.) of silver wire and the cathode of a disk (2.0 cm. diam. × 0.3 cm.) of silver.

The two coulometers which were employed were of the standard dipping electrode type, consisting of a platinum dish containing 15% silver nitrate solution in which a silver electrode was suspended. The coulometers were prepared and employed according to the Bureau of Standards specifications.[25]

The remainder of the electrolytic equipment consisted of standard apparatus: a series of 45-v. batteries, a 750-ohm variable resistance, a 50-ma. meter and a single-pole, single-throw switch.

Constant temperature was maintained during electrolysis by means of a large water-bath equipped with two mechanical stirrers, two 500-watt immersion heaters, and a 200-watt heater regulated by an electronic relay with a mercury thermostat which maintained the desired temperature within ±0.01°. The stirrers and the transference cell were all mounted independently by supports from outside the bath. No observable vibrations occurred in the solutions in the cell. Temperatures were measured at opposite ends of the bath by two thermometers which were graduated in 0.1° intervals and had been accurately calibrated at 0, 32 and 61° by measuring the transition temperatures of water, sodium sulfate decahydrate and strontium chloride hexahydrate. The temperatures at which the experiments were carried out were probably accurate within ±0.05°.

Procedure.—The methods of preparing the electrodes, carrying out the electrolyses, and separating and weighing the solutions were those of Washburn,[24] as modified by Jones and Dole.[26] No novel features were introduced.

The amine salt solutions were electrolyzed with a current of 10 to 45 ma. at a potential of 90 or 135 v. for four to seven hours, depending upon the conductance of each solution. The lower voltage was used for all electrolyses in the Washburn cell in order to keep within the 1 v./cm. potential gradient necessary to prevent gassing at the electrodes.[24] From 0.2 to 0.6 g. of silver was deposited in each coulometer during an electrolysis. The maximum difference between the amounts of silver deposited in the two coulometers during a given electrolysis was 0.12%, the average difference being about 0.05%. Hence, in general, the values which were used in the calculations were considered to be accurate within 0.1%.

Electrode Reactions.—The usual electrode reactions occurred in the Washburn cell. At the anode, silver ions were liberated with the formation of silver chloride, and at the cathode, silver ions from the silver chloride surrounding the electrode were reduced to metallic silver, liberating chloride ions to the solution. Hence, the electrolysis was essentially production of chloride ions at the cathode and the deposition of an identical amount on the anode. The amount of ammonium ion migrating could, thus, be measured directly without the complication of any reaction at the electrodes.

In the smaller cell, hydrogen was liberated at the cathode, while at the anode, a cadmium ammonium complex ion was formed. The formation of this complex had no effect upon the transference numbers of the ammonium ions because at 60° it was soluble in the amounts formed in the solutions investigated. Hence, the complex ion, being larger than the ammonium ion, would be less mobile, and, as found by analysis, no cadmium migrated out of the anode chamber.

Analyses.—Solutions electrolyzed in the Washburn cell were analyzed for both ammonium and chloride ion in the following manner: a known weight (10–20 g.) of amine salt solution was placed in a 600-ml. Kjeldahl flask, the amine was liberated from its salt by excess potassium hydroxide, about 200–300 ml. of water was added, and the amine was steam-distilled through a Kjeldahl trap and condenser into a solution containing a known amount of hydrochloric acid. The amount of ammonium ion in the solution could be ascertained readily by titrating the excess hydrochloric acid in the receiver with standard potassium hydroxide solution, using methyl red indicator. The lower amines steam distill very readily, while hexadecyl- and octadecylamines require considerable amounts of water and distill quite slowly.

The residual solution, from which the amine had been distilled, was washed into a beaker, the excess potassium hydroxide was neutralized with nitric acid, a slight excess of the latter was added, and the solution was analyzed gravimetrically for chloride ion in the usual manner, using fine-sintered Pyrex Gooch crucibles. Analyses for each of the ions could be duplicated within about ±0.2%. This method of analysis was developed after an extended search in order to find a procedure suitable for the determination of both ions in solutions of this type. It was found to give excellent quantitative results upon known samples. The transference numbers calculated from these data are probably accurate to about ±0.8%.

Solutions electrolyzed in the small cell were analyzed only for chloride ion by the Volhard method. It was found that at least 50% more nitric acid was necessary for analyzing the amine salt solutions than is necessary for analyzing inorganic chlorides.[27] The values for chloride

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[24] Washburn, THIS JOURNAL, **31**, 322 (1909).

[25] *Bull. Bur. Standards*, **13**, 479 (1916).

[26] Jones and Dole, THIS JOURNAL, **51**, 1073 (1929).

[27] Treadwell and Hall, "Analytical Chemistry," 9th ed., J. Wiley and Sons, Inc., New York, N. Y., 1942, Vol. II, p. 650.

ion obtained in this manner were accurate to about ±1% and the transference numbers calculated from them are probably accurate to only ±5%. The cationic transference numbers were calculated from the values for the anion, assuming that hydrolysis is negligible. It will be seen below that this assumption was permissible, since the effects of hydrolysis are within the experimental error. The average values of the transference numbers obtained from the smaller cell agreed very well with the later values obtained with the Washburn cell.

Notation.—The following notation will be used in this paper:

N_w, molality
N_v, molarity
d, density of solutions
Ag, gram equivalents of silver deposited in the coulometers
m_+ and m_-, g. equiv. of cation and anion, respectively
M, solution in the middle portion of the transference cell
M_A and M_C, solution between middle and anode portions, and between middle and cathode portions, respectively
A and C, solution in anode and cathode portions, respectively
w, weight of solution in g.
t_+ and t_-, Hittorf transference numbers of cation and anion, respectively
Λ_C, equivalent conductance in mhos at the concentration C (= N_v)
l_+ and l_-, cationic and anionic conductances, respectively, in mhos

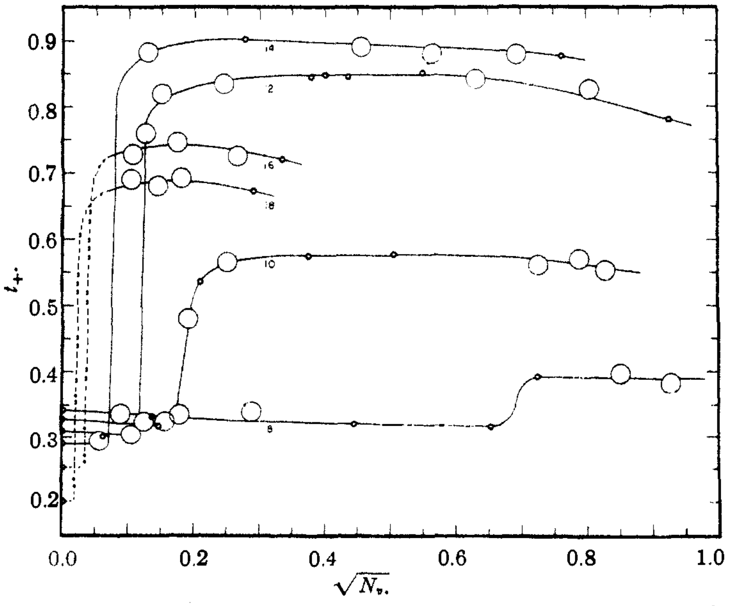

Fig. 1.—Cationic transference numbers of amine hydrochlorides at 60°. The numbers on the curves refer to the number of carbon atoms in the paraffin chains. The circles represent the accuracy obtained with the two transference cells used, the small circles representing the values obtained with the Washburn cell.

The term *transference number* is used broadly in this paper to refer to those fractions of the total current which are carried by the positive and negative components of the amine salt solutions, regardless of the state of dissociation or association of these components. Likewise, the term *ionic conductance* will be used broadly with reference to the conductance of the positive, and of the negative, components of the solutions.

Results

The experimental data for three representative electrolyses in the Washburn cell are tabulated in Table I. These examples show that, as in all of the cases investigated, the salt content of the solution in the middle portion of the cell after electrolysis, when checked against the analytical value of the original solution, was found unchanged. The analytical values in all cases were averages of two or more analyses of each solution. The agreement between the corresponding cationic and anionic transference numbers obtained from the anode and cathode portions of the cell is to be noted. It can be seen that the sum of the cationic and anionic transference numbers of a given solution is unity, within the experimental error shown.

No correction for hydration of the particles has been applied to these values. It has been shown[28] that in dilute solutions an impossible degree of hydration is necessary to change the transference numbers of colloidal electrolytes appreciably, although this effect may be noticeable at high concentrations. However, it was shown[28] that the presence of the reference substance (glycerol) tended to lessen the amount of colloid present in the solutions and hence, the experimental procedure involved is likely to defeat its purpose.

The cationic transference numbers of six amine hydrochlorides in water at 60° are presented graphically in Fig. 1. The abrupt rise to abnormally high values is obvious. This rise occurs at concentrations coincident with the break in the corresponding equivalent conductance curves,[17] *viz.*, C_{10} 0.032, C_{12} 0.013 and C_{14} 0.0045 molar. A break occurs in the cationic transference numbers of

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[28] McBain and Bowden, *J. Chem. Soc.*, 123, 2417 (1923).

TABLE I

TRANSFERENCE NUMBERS OF AMINE HYDROCHLORIDE SOLUTIONS

		$C_8H_{17}NH_2 \cdot HCl$	$C_{12}H_{25}NH_2 \cdot HCl$	$C_{16}H_{33}NH_2 \cdot HC$
Temperature, °C.		60.0	30.0	60.0
N_w		0.580	0.363	0.1175
d		.9756	.9895	.9814
N_v		.526	.333	.1122
$\sqrt{N_v}$		.725	.577	.335
Ag		.004250	.004961	.003072
M	m_+/g. H_2O	.000580	.000363	.0001175
	m_-/g. H_2O	.000580	.000363	.0001174
M_A	w	67.5	69.8	68.8
	m_+/g. H_2O	0.000572	0.000331	0.0001055
	Δm_+	−.00047	−.00193	−.00081
	m_-/g. H_2O	.000573	.000332	.0001058
	Δm_-	−.00041	−.00187	−.00078
A	w	60.7	57.0	57.8
	m_+/g. H_2O	0.000557	0.000313	0.0000921
	Δm_+	−.00121	−.00243	−.00141
	m_-/g. H_2O	.000556	.000312	.0000913
	Δm_-	−.00126	−.00251	−.00144
Total Δm_+		−.00168	−.00436	−.00222
t_+		.395	.879	.723
Total Δm_-		.00258	.00058	.00085
t_-		.607	.117	.277
M_C	w	82.4	85.2	82.0
	m_+/g. H_2O	0.000588	0.000391	0.0001272
	Δm_+	.00057	.00203	.00073
	m_-/g. H_2O	.000589	.000391	.0001267
	Δm_-	.00064	.00203	.00069
C	w	59.4	58.5	58.5
	m_+/g. H_2O	0.000601	0.000409	0.0001445
	Δm_+	.00108	.00229	.00147
	m_-/g. H_2O	.000602	.000410	.0001452
	Δm_-	.00107	.00233	.00151
Total Δm_+		.00165	.00432	.00220
t_+		.388	.872	.717
Total Δm_-		−.00254	−.00060	−.00087
t_-		.598	.121	.283
Average t_+		.392 ± 0.004	.876 ± 0.004	.720 ± 0.003
Average t_-		.603 ± 0.005	.119 ± 0.002	.280 ± 0.003
Λ_C		114.7	35.1	38.1
l_+		45.0	30.8	27.4
l_-		69.2	4.2	10.7

octylamine hydrochloride at about 0.45–0.48 molar, although none was reported for the corresponding equivalent conductance curve. No transference measurements could be made in the vicinity of the critical concentrations of hexadecyl- and octadecylamine hydrochlorides due to their low conductances.

At infinite dilution these cationic transference numbers increase in the following order: C_{18}, C_{16}, C_{14}, C_{12}, C_{10} and C_8. This is the same order in which the equivalent conductances of these salts increase at any given concentration.[17] However, at concentrations beyond the break, the cationic transference numbers increase in the following order: C_8, C_{10}, C_{18}, C_{16}, C_{12} and $C_1{}^4$. This order is identical with that in which the densities of the salts increase at any given concentration.[17]

The transference numbers of the dodecylammonium ion at 20, 30, 40 and 60° are shown graphically in Fig. 2. It can be seen that these values reach a maximum at approximately 40°.

The ionic conductances ($t\Lambda_C$) of three of the salts are presented graphically in Figs. 3, 4 and 5, showing the ionic conductances of octyl-, dodecyl- and hexadecylamine hydrochlorides, respectively, at 60°. An enlarged plot of these values for the octyl-, decyl-, dodecyl- and tetradecylammonium ions in dilute solution is shown in Fig. 6, with the

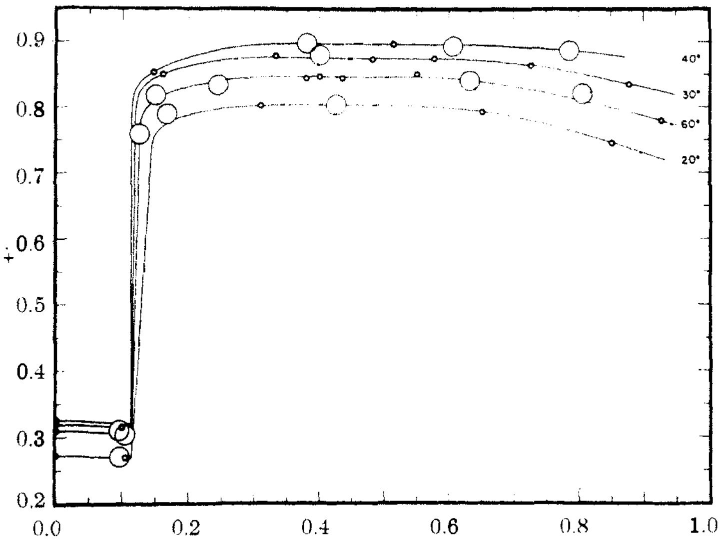

Fig. 2.—Transference numbers of the dodecylammonium ion at 20, 30, 40 and 60°.

corresponding theoretical slopes calculated from the Onsager equation. The latter values were computed with the aid of the recent values[29] for the dielectric constant of water at 60°.

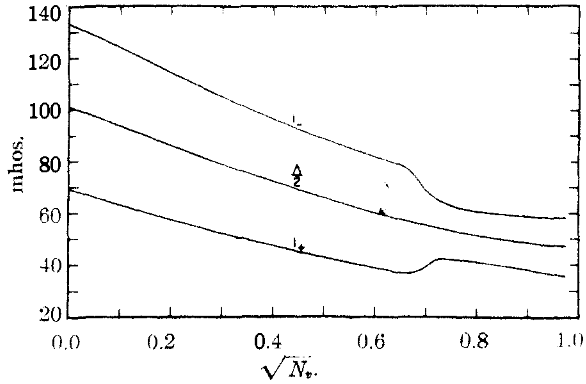

Fig. 3.—Ionic conductances of octylamine hydrochloride at 60°.

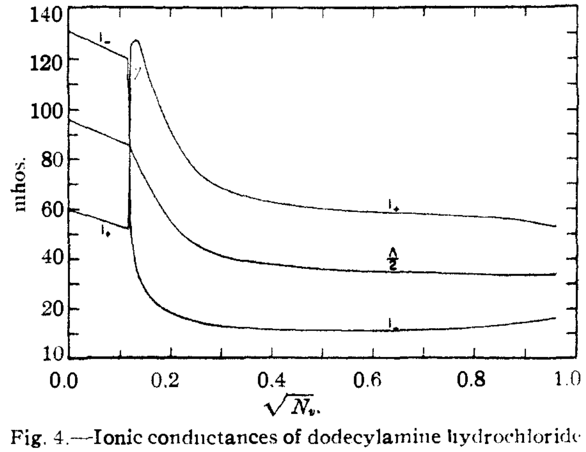

Fig. 4.—Ionic conductances of dodecylamine hydrochloride at 60°.

The variation of pH with concentration is shown graphically in Fig. 7. The curve presented is based upon calculations in the usual manner from the ionization constants of the amines[18] at 25°, and since the latter are essentially the same for all of the normal primary aliphatic amines, the pH curve in Fig. 7 is applicable to all of the salts studied in this investigation. The circles in Fig. 7 represent the experimentally measured pH of dodecylamine hydrochloride at 25°. The values were obtained by determination of the equivalent conductance of a given solution before and after addition of an excess of amine, and calculation of the degree of hydrolysis by the usual equation using Shedlovsky's values for the equivalent conductance of hydrochloric acid.[30] Since these solutions are hydrolyzed to so small an extent, very small experimental errors in measurement of the conductance result in considerable divergence from the values calculated from the ionization constants of the amines.

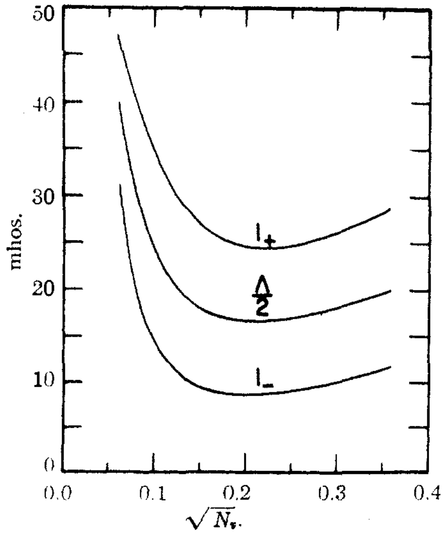

Fig. 5.—Ionic conductances of hexadecylamine hydrochloride at 60°.

Discussion

The behavior of the higher aliphatic amine hydrochlorides in water is characteristic of the col-

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(29) Wyman and Ingalls, This Journal, **60**, 1182 (1938).

(30) Shedlovsky, *ibid.*, **54**, 1405 (1932).

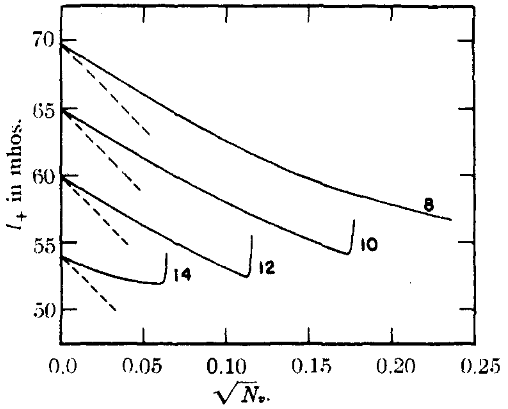

Fig. 6.—Cationic conductances of amine hydrochlorides in dilute solutions at 60°. The numbers on the curves refer to the number of carbon atoms in the paraffin chains.

loidal electrolytes in that the properties of their solutions differ markedly in three fairly distinct ranges of concentration. The following behavior of the salts investigated has been observed, either in the present paper or in those which have been reported previously.

In the first range of concentration the equivalent conductance decreases with increasing concentration in reasonable agreement with the Onsager equation, the actual slopes, in general, being less steep than the theoretical slopes. The cationic transference numbers decrease slightly, while the anionic values show a corresponding rise. The cationic conductance falls, but much less than predicted by the Onsager equation, while the anionic conductance decreases more rapidly than predicted by this equation. The solubility increases very slightly with considerable increase of temperature.

In the second range of concentration the equivalent conductance falls abruptly to a minimum with increasing concentration. The cationic transference numbers rise abruptly to a maximum, while the anionic values correspondingly fall to a minimum. The cationic conductance rises abruptly to a maximum and then falls sharply to a minimum, while the anionic conductance falls abruptly to a minimum. A very slight rise in temperature brings about an abrupt increase in solubility.

In the third range of concentration the equivalent conductance continues to fall with increasing concentration in the cases of octyl- and decylamine hydrochlorides, but rises for the higher homologs, the rise being greater with increasing paraffin chain length. The cationic transference numbers remain constant over a considerable range, but fall off at higher concentrations, more abruptly with higher molecular weight. The anionic transference numbers are, of course, directly the opposite of this behavior. The cationic conductance continues to fall in the cases of the lower amine salts, while for those from the tetradecylamine salt upward in the series, the values increase. In all cases, except that of octylamine hydrochloride, the anionic conductance rises in this range. The solubility continues to increase tremendously with slight rise of temperature, as in the second range. The viscosity, which has, through the first two ranges, been relatively little greater than that of pure water, suddenly increases to extremely high values in this range. The *p*H of the solutions decreases fairly gradually from about 7.0 in very dilute solutions to 5.0–5.5 in the more concentrated solutions.

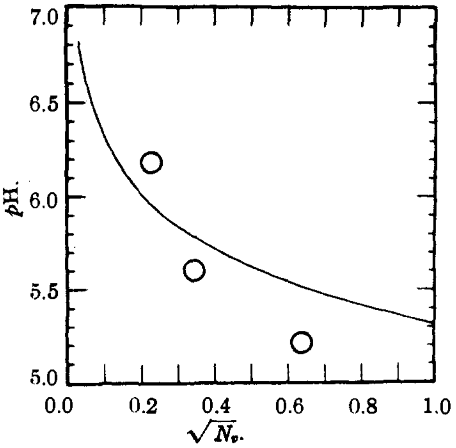

Fig. 7.—*p*H of dodecylamine hydrochloride solutions at 25°.

The apparent inconsistencies in the behavior of these salts can be explained by consideration of the micelle theory. The recent X-ray absorption studies (8–15) have confirmed earlier investigations[31] in which two forms of micelles, differing considerably in size, were separated by ultrafiltration through semi-permeable membranes. The X-ray studies all agree definitely that two different forms of micelles exist in aqueous solutions of colloidal electrolytes. One of these forms is laminiferous, being a crystalline particle consisting of alternate layers of undissociated molecules of paraffin chain salt.[9,11,12,13] This micelle is considerably the larger of the two forms. It would possess very little ability to conduct electrically due to its undissociated nature and any charge that it possesses is merely that of an ordinary

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(31) McBain and Jenkins, *J. Chem. Soc.*, **121**, 2325 (1922).

colloid particle. The other form of micelle is a spherical particle consisting of paraffin chain ions, with the paraffin chains inward and the polar groups at the surface, being, essentially, a minute droplet of liquid crystalline fluid.[11] This micelle would possess high conducting ability due to the fact that its charge would be the sum of the charges of the ions of which it is composed, these charges being concentrated in a relatively smaller volume than occupied by the individual dispersed ions. This is the type of micelle upon which Hartley based his interpretation. Recent measurements[11] of the approximate diameter of this micelle (48 Å.) agree reasonably with the earlier estimates[32] of its size (40 Å.).

In view of the variations among the X-ray studies concerning the structural details of the micelles, it seems evident that there are probably several stages of association and dissociation between the two forms, as well as varying degrees of crystallization. In this way, the disparity among the several interpretations of the micelle theory may be explained.

In recent years, particularly due to relatively general acceptance of the idea of the single type of micelle, the term *ionic micelle* has been gradually abandoned. In view of recent developments, it is evident that this term appropriately designates the small, highly conducting micelles consisting of paraffin chain ions The term *lamellar micelle* is now used to designate the large colloidal aggregates of undissociated molecules, which were formerly called "neutral colloid."

The micelle theory may be briefly summarized by the following generalization: in aqueous solutions, at concentrations above a given critical concentration, colloidal electrolytes exist in two characteristic forms of agglomeration, one being a relatively small, highly charged micelle consisting of paraffin chain ions, and the other being a relatively large, practically neutral, crystalline micelle consisting of laminated undissociated molecules; between these modifications there exists an equilibrium which is dependent upon concentration. With this simplified concept of the micelle theory, the behavior of the amine hydrochlorides can be discussed.

First Range.—In dilute solutions below the critical concentration, these salts behave essentially as simple, completely dissociated univalent electrolytes. However, in view of the fact that the cationic conductances are substantially higher than those predicted by the Onsager equation (Fig. 6), it is evident that some ionic micelles are formed in these dilutions. At the same time, it is evident that some lamellar micelles are produced, removing some of the chloride ions from free ionic dispersion, as shown by the fact that the anionic conductance decreases more rapidly than predicted by the Onsager equation. This agrees with the behavior of other colloidal electrolytes in these dilutions.[7,33]

It will be noted that the cationic conductance of octylamine hydrochloride decreases less rapidly than predicted by the Onsager equation, while this divergence does not appear for the corresponding equivalent conductance.[17] Thus, it is evident that some micellar agglomeration occurs in dilute solutions of this salt. Evidence of micelle formation in solutions of potassium octoate has been reported.[34] This behavior is to be expected, since evidence of micelle formation has been found in solutions of compounds with hydrocarbon chains of only four carbon atoms, *e. g.*, butyric acid.[35]

Second Range.—Although it has been pointed out[7] that it is incompatible with the law of mass action for micelles to form abruptly with increasing concentration, nevertheless, it was found in the investigations of the conductance and transference of the amine salts that a sudden change in these properties occurs at a critical concentration, which marks the beginning of this range. The sharpness of this break has been stressed by numerous investigators.[36–44] At any rate, although both kinds of micelles are, no doubt, formed before the critical concentration, the bulk of the formation occurs beyond the break. The assumption that the equilibrium between the proportion of micelles formed tends, at first, toward the formation of ionic micelles accounts for the sudden increase in cationic transference numbers and cationic conductance. The fact that the highly charged ionic micelles probably attract a consid-

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(32) Hartley, Collie and Samis, *Trans. Faraday Soc.*, **32**, 795 (1936).

(33) Moilliet, Collie, Robinson and Hartley, *ibid.*, **31**, 120 (1935).

(34) Davies and Bury, *J. Chem. Soc.*, 2263 (1930).

(35) Grindley and Bury, *ibid.*, 679 (1929); 1665 (1930).

(36) Lottermoser and Püschel, *Kolloid-Z.*, **63**, 175 (1933).

(37) Bury and Parry, *J. Chem. Soc.*, 626 (1935).

(38) Reed and Tartar, THIS JOURNAL, **58**, 322 (1936).

(39) Hartley, *ibid.*, **58**, 2347 (1936).

(40) Tartar and Wright, *ibid.*, **61**, 539 (1939).

(41) Wright and Tartar, *ibid.*, **61**, 544 (1939).

(42) Wright, Abbott, Sivertz and Tartar, *ibid.*, **61**, 549 (1939).

(43) Tartar and Cadle, *J. Phys. Chem.*, **43**, 1173 (1939).

(44) Haffner, Piccione and Rosenblum, *ibid.*, **46**, 662 (1942).

erable portion of the anions would account for the sudden drop in anionic transference numbers and anionic conductance. No doubt a fraction of the chloride ions is prevented from conducting in this manner, as suggested by Hartley's theory. However, since this would at the same time decrease the conducting power of the ionic micelles, it is more probable that the drop in equivalent conductance and in the transference numbers and conductance of the anion is explained by the concurrent formation of lamellar micelles, rather than by any major "gegen-ion" attraction.

The subsequent fall of the cationic conductance in the second range is occasioned by a shift of the micellar equilibrium toward the formation of a greater proportion of lamellar micelles. Thus, while the equivalent conductance and the conductance of both ions continues to fall, a sufficient percentage of ionic micelles is still formed to maintain the cationic transference numbers at high values. The break in the solubility curves of these salts is also explained by the formation of a large quantity of micelles. This change in the state of dispersion accounts for the tremendous increase in solubility, since a given number of micelles occupy relatively far less space than is required by the number of ions they contain, if the latter were freely dispersed.

Third Range.—The rise of equivalent conductance in this range can be explained, for the lower amines at least, by the increased *p*H of these more concentrated solutions. This increased hydrogen ion concentration, due to hydrolysis, accounts for the decrease in the transference numbers of the ammonium ions, due to the fact that a greater fraction of the current would be carried by the highly conducting hydrogen ion. The effects of hydration of the ionic micelles would be more noticeable in these more concentrated solutions and the values of the cationic transference numbers would decrease. Hydrolysis would also account for the increased transference numbers and conductance of the anion, due to the liberation of chloride ions. However, this explanation does not account for the increased cationic conductance of the higher amine salts, from tetradecylamine hydrochloride upward in the series, where the hydrogen ion concentration is not yet appreciable. There is evidently a shift in the micellar equilibrium toward the formation of a larger proportion of ionic micelles, although this shift cannot be explained any more readily than can that at the critical concentration. At any rate, Hartley's suggestion that the "gegenions" are liberated from the micelles as the concentration increases is not acceptable because of the obvious fact that any dissociation effects are retarded by increased concentration.

The fact that the viscosity of the amine hydrochloride solutions remains very nearly that of water over such a large range of concentration indicates that the formation of micelles alone is not responsible for the sudden increase in viscosity at higher concentrations. This latter effect can be attributed to the formation of irregular aggregates of lamellar micelles which are beginning to assemble the framework of the gel state, which occurs as the concentration is further increased. These irregular aggregates enmesh quantities of solvent (or solution), thus creating a high structural viscosity.[14,15,45]

Summary

The transference numbers in water at 60° have been determined for the normal primary aliphatic amine hydrochlorides containing 8, 10, 12, 14, 16 and 18 carbon atoms in the paraffin chain, with additional transference numbers of the dodecylammonium ion at 20, 30 and 40°.

The behavior of these salts in aqueous solution has been discussed in terms of the recent developments of the micelle theory.

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(45) McBain, *J. Phys. Chem.*, **30**, 239 (1926); McBain, Willavoys and Heighington, *J. Chem. Soc.*, 2689 (1927).