

CONDUCTIVITY OF CERTAIN SALTS IN ETHYL AMINE.

BY EDWARD G. MAHIN.

The conductivities of silver nitrate, lithium chloride and ammonium chloride in ethyl amine were measured by Shinn,¹ who showed that the molecular conductivities change with dilution in an unexpected manner. In the case of silver nitrate the molecular conductivity decreases with dilution until $V=75.15$, this being the highest dilution used. The molecular conductivity of lithium chloride increases with dilution until $V=0.867$, then decreases until $V=21.08$, after which it apparently slightly increases. The molecular conductivity of ammonium chloride decreases with dilution until $V=18.24$, after which it increases. These facts would not seem remarkable were it not for the concluding words of the author's paper. After summarizing the results of his experimental work, he says:

"From the standpoint of the theory of electrolytic dissociation the electrical behavior of solutions in primary and secondary amines and in amides, so far as such solutions have been studied, is inexplicable. The facts that for one and the same solute the conductivities of solutions may not only be very large or very small, but may increase or decrease with dilution, or attain maximum or minimum values depending upon the specific nature of the solvent, suggest that the role of the solvent in the process of the transmission of an electric current through a solution is, in all probability, a very active rather than an indifferent one, and does not materially differ from that of the solute. In such event, the prevalent conception of 'molecular conductivity' becomes not only meaningless, but misleading."

In arriving at the conclusions here indicated it would seem that the author has overlooked certain facts which may not only serve to explain the apparent departure from the dilution laws, but which would make this departure seem inevitable. It has long been known that the aliphatic amines are strongly basic substances, forming simple salts analogous to the ammonium salts, as well as complex metallic salts which are analogous to those where hydrogen of the ammonium radicle is substituted by a metal. Indeed, this salt formation is to be expected since the ali-

¹ J. Phys. Ch., *11*, 537.

phatic primary amines are members of a series of mono-substituted ammonias, of which the basicity is greater than that of the mother substance.

Köhler¹ isolated a salt having the composition represented by the formula $C_2H_5NH_2.HgCl$. Müller² investigated double salts of ethyl amine with palladium, Jorgensen³ those with platinum, Carson and Norton⁴ those with uranium, Bailey⁵ with vanadium, Bonnefoi¹ with lithium chloride, and Hoffman and Marburg⁷ with mercuric chloride. In most cases more than one salt was produced by varying the proportions of ethyl amine and the simple salt used. Hoffman and Marburg isolated and studied the compounds $C_2H_5NH_2.HgCl_2$, $(C_2H_5NH_2)_2.HgCl_2$ and $C_2H_5NH.HgCl$. Bonnefoi found that by leading the vapor of ethyl amine over dry lithium chloride various double salts were produced, the proportion of the constituents depending upon the temperature. The following compounds were formed under the conditions indicated:

<i>Temp.</i>	<i>Formula.</i>	<i>Heat of Formation, Calories.</i>
70°	$C_2H_5NH_2.LiCl$	+ 13834
58°-70°	$(C_2H_5NH_2)_2.LiCl$	+ 24817
Ord. to 58°	$(C_2H_5NH_2)_3.LiCl$	+ 35387

It seems probable, in the light of these facts, that at still lower temperatures other compounds will be present, having a still higher ratio of ethyl amine to the original salt; this should be particularly true with regard to solutions in liquid, anhydrous ethyl amine. In other words, we are here dealing with an application of the mass law, where the temperature and mass of the reacting substances are to be considered in the attempt to solve the problem regarding the composition of the resulting compound. We should expect that any solution would contain several compounds of the constituents, having a certain average composition which would depend upon the temperature and degree of dilution.

Shinn⁸ tested, in an approximate but not quantitative manner, the action of ethyl amine upon 14 salts, concerning which the following résumé is here given:

¹ Ber., 12, 2323.

² Ann., 86, 366.

³ J. pr. Ch., (2) 33, 517.

⁴ Am. Ch. J., 10, 220.

⁵ J. Ch. Soc., 45, 693.

⁶ C. r., 129, 1257.

⁷ Ann., 305, 191.

⁸ Loc. cit.

NH_4Cl . . . Very soluble with evolution of ammonia.
 LiCl . . . Soluble.
 FeCl_3 . . . Slightly soluble.
 SnCl_2 . . . Insoluble, unchanged.
 CoCl_2 . . . Reacts with evolution of heat, forming greenish yellow precipitate.
 PbBr_2 . . . Reacts, forming white precipitate which afterward redissolves.
 KI . . . Insoluble, unchanged.
 CdI_2 . . . Reacts, forming white, insoluble precipitate.
 AgCN . . . Slightly soluble.
 $\text{Hg}(\text{CN})_2$. . . Slightly soluble.
 AgNO_3 . . . Soluble with evolution of much heat.
 NaNO_3 . . . Insoluble, unchanged.
 $\text{Pb}(\text{NO}_3)_2$. . . Reacts, forming white, insoluble precipitate.

It is thus seen that, in all cases where the salt dissolves appreciably, there is evidence of chemical action, either through the evolution of heat or the formation of a precipitate, or both. In the case of ammonium chloride the well known action of evolution of ammonia was observed. There is, therefore, every reason for expecting that complex salts will be formed in every case excepting the last, where no doubt ethyl amine hydrochloride is produced, as Shinn has pointed out. If this be true, the question still remains as to whether the reaction is complete as soon as the salt is all in solution, so that henceforth all physical properties will be those of a solution in ethyl amine of a definite double or complex salt, changing with dilution only with respect to the degree of ionization. With the investigations of Hofmann and Marburg and of Bonnefoi in mind, the answer to this question would certainly be negative. We should expect that the ratio of ethyl amine to simple salt combined with it would not only change with lowering of temperature, but that it would increase with decreasing concentration, because as dilution progresses the ratio of amine to salt in solution increases. If the conductivity of the complex salt is much less than that of the simple salt the change in molecular conductivity with change in concentration would be the resultant of two influences, i. e., change in ionization and change in complexity of the ions. The migration velocity of a complex cation containing one or more molecules of ethyl amine could not be very high, and it is not likely that such a compound would possess a very high degree of ionization. This fact would then result in a more or less gradual tendency toward falling off in the molecular conductivity with increasing dilution, since we are actually dealing not only with more complex compounds, whose ioniza-

tion is probably less than that of the simpler ones, but also with more complex ions, whose velocity is probably less than that of the simpler ones. If, however, the ionization resulting from dilution proceeds at a greater rate than does the change in complexity, increase in molecular conductivity would then be the rule. This actually happens for a certain range in the case of lithium chloride, then later the increasing complexity of the ions perhaps gains the ascendancy and molecular conductivity decreases with further dilution. The effect of dilution upon molecular conductivity will necessarily be somewhat complicated, if the preceding reasoning is correct, involving at least the following changes: (a) Increase in molecular complexity, through increase in the active mass of ethyl amine. (b) change (probably decrease) in *ionization constant* because of increasing complexity, (c) increase in ionization of any one form, since at any dilution a considerable number of different complexes are probably present, and (d) probable decrease in migration velocity on account of increasing complexity of the ions.

This would seem to be merely another special case of the influence of solvate formation upon conductivity, and such influences have long been known. The formation of hydrates, for example, has a very marked effect upon the conductivity and upon the lowering of freezing point and vapor pressure of aqueous solutions.

In the case of solutions of ammonium chloride in ethyl amine it is by no means certain that the entire amount of salt is converted at once into ethyl amine hydrochloride when brought into a solution of any concentration. We should certainly expect that equilibrium will result when a certain amount of ammonium chloride remains as such in the solution, this amount becoming smaller as dilution proceeds. The molecular conductivity will then depend upon (a) the ratio of ethyl amine hydrochloride to ammonium chloride, (b) the relative ionization constants of the two compounds and (c) the relative migration velocities of the two (or more) cations involved.

The theory of electrolytic dissociation has proven of so great value to physical chemistry and has piloted the way to so many valuable investigations that one cannot fail to realize its importance. This does not mean that its imperfections should be ignored or that there should be any cessation in the search for facts which will test it to the extreme. But so many supposed objections have been urged against it that, on closer

investigation, have been found to entirely conform to the theory or to require only minor modifications, that we hesitate to accept such a sweeping statement as that contained in Shinn's paper. The facts cited do not necessarily conflict with the theory—indeed, they would seem to point to the truth of the theory. What is needed is more experimental evidence covering these points.

Purdue University,
Lafayette, Ind.

