CX.—*The Dissociation of Salts in Nitrobenzene.*

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The systematic study of electrolytic solutions has shown that they may be divided broadly into two classes: (*a*) strong electrolytes, including most salts, and (*b*) weak electrolytes, consisting mainly of acids and bases. In general, the typical strong electrolytes retain their strength in most solvents, whereas acids and bases vary considerably in strength from one solvent to another in a manner determined largely by the acid and basic properties of the solvents. Of recent years, however, more careful examination of individual salts, mainly by Walden and Hartley and their respective collaborators and also by Martin (J., 1928, 3270), has shown that even salts vary considerably in their behaviour when solvents other than water are employed. For the majority of salts these variations seem to be highly specific, rendering very uncertain any exact prediction of the behaviour of a salt in a given solvent; but it has been found by Walden for one class of salts, *i.e.*, the tetra-substituted ammonium bases, that it is possible to make such a prediction, since the behaviour of these salts conforms fairly closely to the Onsager equation for electrical conductivity; *i.e.*, their behaviour is determined by the physical properties of the solvent. Such a behaviour is perhaps to be expected when one considers the similarity between the organic kations of these salts and the solvents in which measurements have been made; nevertheless, it is surprising that Walden has made the further observation that the salts of the partially-substituted ammonium bases in no way conform to the normal behaviour exhibited by the fully substituted salts, but, on the contrary, become extremely weak electrolytes even in certain solvents of high dielectric constant. In view of the intrinsic importance of this discovery and its bearing on the study of acids and bases, it seemed desirable to investigate the behaviour of salts of this type in nitrobenzene and to attempt an elucidation of the causes of their peculiarities.

EXPERIMENTAL.

The nitrobenzene was shaken with caustic soda and twice distilled under about 10 mm., the second distillation being from phosphoric oxide; its resistance in the conductivity cell was comparable with that of the insulation, so the specific conductivity was not greater than 10^{-8} mho.

The salts were prepared by mixing various acids and bases, all of which were either the purest obtainable commercially or were carefully purified. No particular precautions were taken to purify the salts after preparation, but they were dried in a vacuum over phosphoric oxide.

The conductivity measurements were made by the method of Frazer and Hartley (*Proc. Roy. Soc.*, 1925, **109**, *A*, 351) and the cell employed was of the Hartley and Barrett type (J., 1913, **103**, 789) but designed to hold about 50 c.c. instead of 250 c.c.; the constant, referred to Kohlrausch's data for potassium chloride, was 0·1735. All measurements were made at 25°.

Results.—The results are summarised in Table I. The concentrations, C, are expressed in g.-equivs. per litre, the density of the solutions being assumed to be identical with that of the pure solvent, *viz.*, 1·198 at 25°. The equivalent conductivities, Λ, are expressed in reciprocal ohms.

TABLE I.

Dipropylamine picrate.		Piperidine picrate.		Diphenylguanidine picrate.		Piperidine perchlorate.		Dipropylamine perchlorate.	
$C \times 10^4$.	Λ.	$C \times 10^4$.	Λ.	$C \times 10^4$.	Λ.	$C \times 10^4$.	Λ.	$C \times 10^4$.	Λ.
2·026	17·99	1·399	21·04	1·655	9·51	2·667	34·45	1·615	33·56
4·193	14·89	2·797	17·24	3·514	7·15	6·019	32·05	3·922	31·15
9·352	11·23	5·082	14·13	9·140	4·73	11·938	29·04	8·189	28·03
16·955	8·86	8·604	11·70	18·128	3·48	20·06	26·28	12·24	25·95
28·07	7·24	15·882	9·25	33·58	2·63	40·32	22·21	26·86	21·42
42·96	6·09	29·04	7·24	*32·78	5·10	*39·38	25·60		

* These figures refer to solutions containing 1·47% of ethyl alcohol.

An attempt was made to measure the conductivities of solutions of dipropylamine and piperidine chlorides and dipropylamine trichloroacetate, but the resistances were too great to allow of accurate measurement.

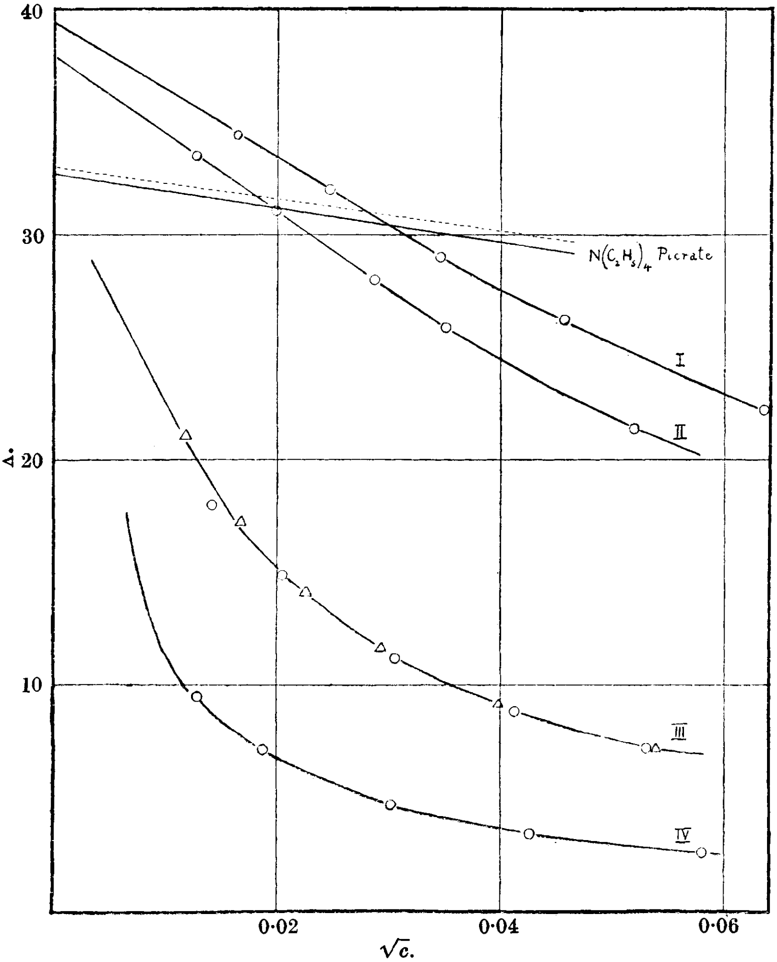
Discussion of Results.

The results are plotted in the figure together with the data of Murray-Rust, Hadow, and Hartley (this vol., p. 215) for tetraethylammonium picrate; the broken line represents the theoretical slope according to Onsager's equation,

$$\Lambda = \Lambda_0 - (0{\cdot}784\Lambda_0 + 44{\cdot}2)c^{\frac{1}{2}}$$

the dielectric constant of nitrobenzene being assumed to be 34·5 and its viscosity 0·0183 : it is evident that all the salts investigated are definitely weak electrolytes, whereas the tetraethylammonium salts are strong electrolytes. It is also noticeable that the perchlorates are stronger than the picrates, and these, in turn, are much stronger than the chlorides, which are extremely weak electrolytes. Calculation of the dissociation constants gives for the two perchlorates values of 2—3 × 10^{-3}, for dipropylamine and piperidine picrates 1·7 × 10^{-4}, and for diphenylguanidine picrate 2·2 × 10^{-5}. Correction for the interionic forces, the validity of Onsager's and Debye and Hückel's equations being assumed, does not greatly improve the constancy of the values.

FIG. 1.



I. *Piperidine perchlorate.* II. *Dipropylamine perchlorate.*
III. △ *Piperidine picrate.* ⊙ *Dipropylamine picrate.*
IV. *Diphenylguanidine picrate.*

It would be possible to explain the weakness of these salts by assuming that they are largely dissociated into the free acid and base, but, as has been clearly shown by Walden, Ulich, and Busch (*Z. physikal. Chem.*, 1926, **123**, 429), there are conclusive arguments against such an assumption. The most cogent of these are : (1) As picric acid is a weaker acid than hydrochloric, the picrates should be the ' weaker ' salts. (2) An equilibrium of the type $B + HA = BH^{\cdot} + A'$ shoud not be influenced very much by the concentration and, consequently, the form of the equivalent conductivity curve should be the same as for the typical strong electrolytes. (3) Walden has shown that there is no free hydrochloric acid in the chloride solutions. (4) The same author has shown that the conductivity is not affected by additions of the free acid or base.

We can only conclude, therefore, that the salts of the partially-substituted ammonias are constitutionally weak electrolytes, and that they all exist to a greater or less extent in the form of non-ionic molecules. In order to explain the existence of such non-ionic molecules, it seems simplest to adopt the suggestion put forward by Moore and Winmill (J., 1912, **101**, 1635) and by Pfeiffer (*Annalen*, 1913, **398**, 152) and later elaborated by Latimer and Rodebush (*J. Amer. Chem. Soc.*, 1920, **42**, 1419) that hydrogen can exert a covalency of 2. This suggestion was first advanced in order to account for the weakness of aqueous solutions of ammonia, but there the alternative explanation is still possible that no ammonium hydroxide molecules exist in the solution, for in their work, Moore and Winmill made assumptions which are open to criticism particularly in view of the recent work of Lannung (*J. Amer. Chem. Soc.*, 1930, **52**, 68). While this conception of bicovalent hydrogen has hitherto been restricted to compounds in which this atom is linked to a fluorine or an oxygen atom, there seems no reason why other atoms should not behave similarly; in particular we might expect chlorine, whose general behaviour is closest to that of fluorine, to have a similar effect in this respect also. It is indeed significant that, of the salts we are considering, the chlorides are quite the weakest, the bromides, according to Walden, being markedly stronger, and the iodides much stronger still.

If it is correct to formulate these salts in the way suggested, then certain consequences may be expected. In the first place, if the salt itself can exist in a non-ionic form, its ionisation will be greatly assisted when the solvent can in some way interact with the ammonium ion and separate it from the anion ; thus we may write

$$R_3N{:}H{:}Cl + S = [R_3N{:}H{:}S]^{\cdot} + Cl'$$

where $R_3N{:}H{:}Cl$ represents the salt, and S the solvent molecule. Actually, it is found that these salts function as strong electrolytes only when dissolved in the hydroxylic solvents, water, methyl and ethyl alcohols *; in nitrobenzene, acetonitrile, acetone, ethylene chloride, dichloroethylene, and tetrachloroethane, and also in the fused state, they are weak electrolytes in spite of the fact that the dielectric constants of the first three members of this group are comparable with those of the alcohols. Furthermore, the addition of ethyl alcohol to the solutions of these salts in nitrobenzene causes a considerable increase in the conductivity as shown in Table I. It is noteworthy that the conductivity of piperidine perchlorate is less affected by the addition of alcohol than that of the weaker electrolyte diphenylguanidine picrate, and moreover, an approximate measurement showed that dipropylamine chloride is even more markedly affected. These observations are quite analogous to those of Goldschmidt on the effect of addition of water on the conductivity of weak acids in the alcohols, and the explanation here advanced is the same as his.

If solvation of the substituted ammonium ions is a necessary prelude to the ionisation of their salts, then we should expect to find evidence of such solvation in the hydroxylic solvents where ionisation is apparently complete. As a rule, evidence for solvation is not convincing because of theoretical objections to the methods employed, and this is particularly true of the calculation of solvation values from ionic mobilities; here, however, by comparing the mobilities of structurally similar ions, we can arrive at conclusions with some assurance.

If we consider the ammonium and the tetramethylammonium ion, then, on the views outlined above, these ions in aqueous solutions will be $N(OH_3)_4^{\cdot}$ and $N(CH_3)_4$ whereas in methyl alcohol the ammonium ion will become $N(CH_3{\cdot}OH_2)_4^{\cdot}$. We cannot with certainty predict whether the OH_3 group is larger than the CH_3 group or not, but the atomic volume of oxygen is less than that of carbon, so it is not surprising to find that the mobility of the ammonium ion in water is 75·0 whereas that of the tetramethylammonium ion is 46·5. In methyl alcohol, however, we should certainly expect the ion $N(CH_3{\cdot}OH_2)_4^{\cdot}$ to be larger than the ion $N(CH_3)_4^{\cdot}$, and in agreement with this the mobilities of the ammonium and the tetramethylammonium ion are 58·3 and 66 respectively. Similarly, in ethyl alcohol the mobilities of the two ions are 22 and 29·3.

On the basis of Walden's data (*Z. physikal. Chem.*, 1929, **144**, 269) it is possible to test our hypothesis further by comparing the mobilities of the ethyl-substituted ammonium ions in the alcohols

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* According to Goldschmidt's data for piperidine hydrochloride in *iso*butyl alcohol (*Z. physikal. Chem.*, 1926, **124**, 23), we may include this solvent as well.

and in acetonitrile, a non-hydroxylic solvent, where solvation should not occur :

Mobilities of substituted ammonium ions at 25°.

	Aceto-nitrile.	Ethyl alcohol.	Methyl alcohol.
$N(C_2H_5)H_3^{\cdot}$	99	—	—
$N(C_2H_5)_2H_2^{\cdot}$	94	25·8	51
$N(C_2H_5)_3H^{\cdot}$	87	—	—
$N(C_2H_5)_4^{\cdot}$	86	26·9	54

The reversal of the order of the mobilities with change from the non-hydroxylic to the hydroxylic solvents is very striking and confirms our views.

A further test is afforded by the mobilities of isomeric ions; it was first suggested by Ostwald that the mobilities of such ions are identical, and considerable support is given to this view by the data for organic anions, but it has been shown by Walden and Ulich (*Z. physikal. Chem.*, 1924, **114**, 317) that the rule does not apply to the substituted ammonium ions. Ostwald's idea, however, seems quite reasonable, and it is possible to explain Walden's results on the basis of solvation; thus we should expect to find that in non-hydroxylic solvents isomeric ions possess the same mobility, whereas in hydroxylic solvents the partially substituted ammonium ions would be solvated and consequently have lower mobilities. This is borne out by Walden's data for three isomeric ions, the *iso*butylammonium, the diethylammonium, and the tetramethylammonium ions :

Mobilities of isomeric ions at 25°.

	Aceto-nitrile.	Acetone.	Ethyl alcohol.	Methyl alcohol.	Water.
$N(C_4H_9)H_3^{\cdot}$	90	92	20·9	47	31·4
$N(C_2H_5)_2H_2^{\cdot}$	94	92	25·7	56	32·2
$N(CH_3)_4^{\cdot}$	93	102	29·5	66	39·7

The only anomaly is the somewhat high mobility of the tetramethylammonium ion in acetone, and this may in part be due to errors in Λ_0 because the Λ–$c^{\frac{1}{2}}$ curves in acetone are very steep and render extrapolation somewhat uncertain. Even assuming the values given to be quite accurate, the difference between the mobilities of the tetramethylammonium and the *iso*butylammonium ions in acetone is only 10%, whereas in the alcohols it is 40%, and in water 25%.

The behaviour of these salts has important bearings on the study of acids and bases in non-hydroxylic solvents. In the first place, it renders invalid the conductivity method for comparing the strength of acids, since the assumption made in applying the method is that the sole reaction occurring in solution is $HA + S = HS^{\cdot} + A'$, where HA is the acid, S the solvent molecule, $HS^{\cdot}$ the solvated hydrogen ion, and A' the anion, but in non-basic solvents this reaction does not occur and the acid will instead react with any water present,* thus $HA + H_2O = OH_3A$. Now OH_3A is a compound analogous to NH_4A, and consequently we should expect it to be a weak electrolyte; also, from the results presented here, we should expect oxonium perchlorate (OH_3ClO_4) to be a stronger electrolyte than oxonium chloride (OH_3Cl) and in consequence a solution of perchloric acid in a non-hydroxylic solvent should be a much better conductor of the electric current than a corresponding solution of hydrogen chloride quite irrespective of which is the stronger acid.

Secondly, it affects the use of buffer solutions of which salts of the ammonium type are constituents. The importance of this can be understood when it is realised that not many common electrolytes are soluble in non-hydroxylic solvents, particularly those of low dielectric constant, and amongst the most readily accessible substances are the substituted ammonias and their salts.

Summary.

1. Measurements have been made of the conductivities of various salts in nitrobenzene.

2. The behaviour of these salts has been explained on the assumption that they exist in a non-ionic form.

3. Evidence in favour of the assumption is advanced from the mobilities of the ion.

4. The bearing of these results on the study of acids and bases is discussed.

I wish to express my thanks to Sir Harold Hartley, F.R.S., for allowing me to carry out these measurements in the Balliol and Trinity College laboratories, and I particularly wish to thank Mr. D. M. Murray-Rust for his help in making the measurements.

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* That this is not a remote possibility is shown by the fact previously emphasised that a 0·01% solution of water corresponds to a normality of 0·005 (Wynne-Jones, *J. Physical Chem.*, 1927, **31**, 1653).