

IONIC INTERACTION, DISSOCIATION AND MOLECULAR STRUCTURE

BY O. REDLICH AND G. C. HOOD

Shell Development Company, Emeryville, California

Received 24th June, 1957

For the determination of the degree of dissociation of nitric, perchloric, sulphuric and trifluoroacetic acids, various data (Raman intensities, magnetic resonance of the H, N, Cl, F nuclei obtained by several authors) are available. New measurements of the nuclear magnetic resonance of sulphuric and heptafluorobutyric acids have been added. The results are in very satisfactory agreement. These acids present, therefore, an opportunity for testing other methods of determining degrees of dissociation of strong electrolytes.

The following deductive pattern has been recurring in the theory of solutions during the last fifty years: the validity of some limiting law is experimentally established in a certain concentration range and assumed beyond this range; deviations are interpreted as indicating chemical changes such as solvation or incomplete dissociation. The uncertainties inherent in this pattern are discussed in an example.

THE DISSOCIATION OF STRONG ACIDS

The problem of the dissociation of the strong electrolytes in aqueous solutions, unsolved for 50 years after Arrhenius' discovery, has finally become a subject of regular and progressing investigation. The agreement between the results of different methods and observers justifies considerable confidence that the description of the dissociation of nitric, sulphuric, perchloric, trifluoroacetic and heptafluorobutyric acids is essentially correct.

TABLE 1.—DISSOCIATION CONSTANT K OF NITRIC ACID

method	K	observation	calculation	ref.
dielectric const.	40		Wynne-Jones (1933)	1
colorimetric	>20	Halban, Seiler (1937)		2
u.-v. extinct.	9	Halban, Eisenbrand (1928)	Redlich (1938)	3, 11
	7	Coryell, Goldring (1955)		6
Raman	1.9	I. R. Rao (1930)	R., Rosenfeld (1936)	8, 11
	1.2	Simons (1933)	"	9, 11
	24	Chédin (1937)	Redlich (1938)	10, 11
	21	R., Bigeleisen (1943)		13
	23.5	Young, Krawetz (1955)		4
n.m.r.	22	H., R., R. (1954)		17

The development of the problem is illustrated by the various results obtained for the thermodynamic dissociation constant of nitric acid (table 1). The table does not contain early wild and unjustified guesses. But the early estimate of Wynne-Jones,¹ while crude, was entirely reasonable: it was obtained by an extrapolation from non-aqueous solutions, based on the assumption that the logarithm of the dissociation constant is a linear function of the reciprocal dielectric constant. Halban and Seiler² did not find any deviation from complete dissociation by

colorimetric determination of the hydrogen ion concentration. But their procedure, though extremely refined, was still not accurate enough to find a deviation constant greater than about 20.

The first reasonable attempt at a genuine measurement of the dissociation of a strong electrolyte was the careful investigation of light absorption by nitric acid in the ultra-violet by Halban and Eisenbrand.³ Unfortunately, the environment of an ion or molecule influences extinction coefficients so much that they cannot quite safely be relied upon as a basis for the determination of concentrations.⁴ Indeed, Halban and Eisenbrand as well as Dalmon,⁵ and Coryell and Goldring,⁶ found less dissociation than has been derived by other methods. The failure of ultra-violet absorption is illustrated by the fact that the molal heat of dissociation has been found⁶ to be

$$H(\text{undiss.}) - H(\text{ions}) = -1.1 \text{ kcal}, \quad (1)$$

so that dilution of concentrated nitric acid would entail cooling. From calorimetric data one concludes⁷ that the value must be somewhere between +2 and 5 kcal.

There exists good evidence that the intensity of Raman lines quite generally depends much less on the environment than do the extinction coefficients. The relation between concentration and intensity of the strongest Raman line of the nitrate ion has been studied by several observers and most carefully by Young and Krawetz.⁴

The older measurements on nitric acid^{9, 10} suffered from the lack of a calibration of the specific intensity of the nitrate line used. A bold extrapolation procedure used by Redlich and Rosenfeld¹¹ could not furnish reliable results. The same authors, however, also suggested the comparison of the intensities of the nitrate line in solutions of sodium nitrate and nitric acid. By this method, Rao¹² and Redlich and Bigeleisen¹³ obtained the first reliable, though still crude results. A new level of accuracy was reached by Young,^{4, 14} and his co-workers, particularly by the introduction of photoelectric intensity measurement.

Nuclear magnetic resonance is in some respects even superior to the intensity of Raman lines. The "chemical shift" of a nuclear magnetic resonance frequency indicates how much a strong external magnetic field, acting on a nucleus, is altered by the environment of the nucleus. The alteration is due almost exclusively to nearby electrons, i.e., to the adjacent bonds and atoms. The influence of the extramolecular environment is corrected with the aid of the magnetic susceptibility of the solution. This correction does not take into account any order around the molecule such as produced by an ionic atmosphere, but the correction itself is small and therefore presumably sufficiently accurate.

The proton resonance in aqueous solutions is, in addition, influenced by the concentration dependence of hydration and association. This effect expresses itself in small differences in the concentration dependence of the shift in dilute acids (HNO_3 , HClO_4 , HCl). It is in first order automatically eliminated by the observations. Such a source of error does not exist if the solvent does not contain the observed nucleus.

On the whole, the shift of n.m.r. satisfies very well the fundamental requirement, namely, that the observed effect should be independent of extramolecular influences. It is inferior to Raman intensities only in being a colligative property, as far as the present application is concerned. The observed shift is an average of the shifts of ions and undissociated molecules, weighted by their concentrations. It furnishes, therefore, less information than the Raman intensity, which is a specific property of a single species and thus most suitable as a primary method.

The influence of incomplete dissociation on n.m.r. was established by Masuda and Kanda¹⁵ and by Gutowsky and Saika.¹⁶ Subsequent measurements of the proton resonance¹⁷ turned out to be in complete agreement¹⁸ with the Raman intensities of Young and Krawetz.⁴ The nitrogen resonance results of Masuda

and Kanda are also in sufficient agreement (fig. 1) with the proton resonances¹⁷ if the calculation of both sets of degrees of dissociation is based on the approximately correct assumption that a solution of the composition $\text{HNO}_3 \cdot \text{H}_2\text{O}$ is practically undissociated.

According to Young and Krawetz,⁴ nitric acid is a weak electrolyte at high temperatures so that conductivity data above 200°C can be combined with their data to give a complete description of the dissociation of nitric acid between 0 and 300°C . Their heat of dissociation is well within the range suggested by the heats of dilution.⁷

The rapid increase of the activity coefficient of the undissociated molecule with the concentration has always been interpreted as a salting-out effect of the kind explained by Debye and McAuley.¹⁹ McKay²⁰ splits the observed activity

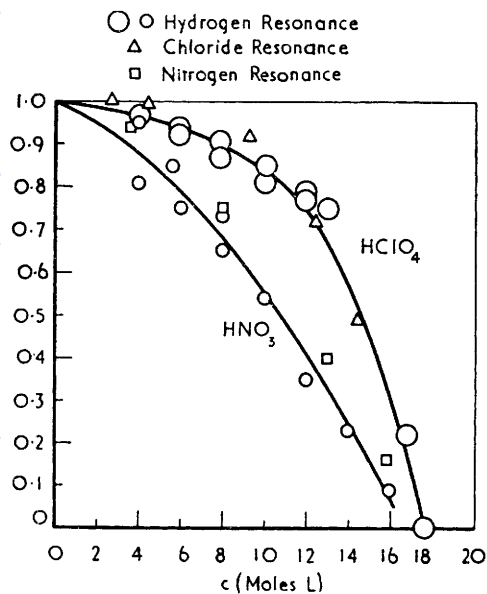


FIG. 1.—Degree of Dissociation of HNO_3 and HClO_4 from N.M.R.

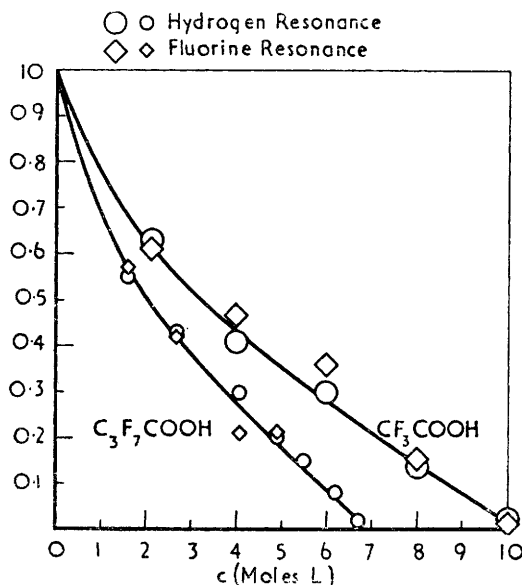


FIG. 2.—Degree of Dissociation of CF_3COOH and $\text{C}_3\text{F}_7\text{COOH}$ from N.M.R.

coefficient of nitric acid into a factor which follows the rule of Åkerlöf and Thomas²¹ and a factor determined by the salting-out effect. The order of magnitude of the coefficients derived is reasonable (McKay's result for the dissociation constant is in agreement with previous calculations. It is hardly more accurate since the uncertainty is merely shifted from the actual extrapolation to the assumption of strict validity up to high concentrations of the relations of Åkerlöf and Thomas, and of Debye and McAuley).

Degrees of dissociation obtained by different methods also agree very satisfactorily for other acids. Earlier¹⁶ and recent²² determinations of the proton magnetic resonance of sulphuric acid over the whole concentration range are in full accord with Young's Raman intensities.¹⁴ The results derived for perchloric acid from proton¹⁷ and chlorine²³ resonances are in satisfactory agreement (fig. 1) with each other and with Raman intensities.²⁴ Earlier measurements on trifluoroacetic acid²⁵ and new ones on heptafluorobutyric acid²⁶ furnish concordant results for the degree of dissociation (fig. 2).

Dissociation constants at 25°C of several acids are shown in table 2. For a comparison, the values derived by Henne and Fox²⁷ from their conductivities

according to Ostwald's law are given in parentheses. Young and Jones²⁸ pointed out that Ostwald's law cannot give even an approximation of the correct value. This is well illustrated by the n.m.r. results.

TABLE 2.—DISSOCIATION CONSTANTS OF STRONG ACIDS

acid	K	ref.
perchloric	38	17, 24
nitric	23.5	4
trifluoroacetic	(0.588)	27
	1.8	25
heptafluorobutyric	(0.678)	27
	1.1	26

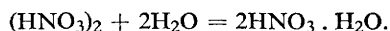
The body of information developed for the strong acids during the last 20 years appears to be consistent and quite satisfactory. It is based on what are believed to be sound concepts and reliable experimental methods. There are now sufficient independent checks to justify confidence in the data and their interpretation. The results depend in no way on a theory or assumption regarding activity coefficients and conductivities.

MOLECULAR STRUCTURE

It happens quite often that an inherently useful and fertile idea is stretched on a Procrustean bed until it loses its original vigour and value. Nowhere has this been done more frequently or more persistently than in the molecular theory of solutions. It was a perfectly sound and valuable idea to explain specific anomalies in thermodynamic and other properties of solutions by the formation of compounds or complexes. But there has always been a great temptation to explain every deviation from a perfect solution by compound formation. In spite of all modern refinements, the danger is as great as ever.

It is here that Raman and infra-red spectra show their specific value. As a rule, the spectra are sufficiently well interpreted. Thus we know that the intensity of a line or band really measures the concentration of a certain compound or non-associated alcohol and so on, and not some entirely different effect. We are not quite on equally safe ground with ultra-violet spectra, which are not so safely interpreted. Still less suitable as primary evidence are colligative properties such as nuclear magnetic resonance, thermodynamic properties and refractivity. There are large effects, of course, for instance in the heat of dilution or the molal volume, that are unquestionably interpreted as due to a chemical change. But the quantitative interpretation, particularly of a second-order effect, as an indication of chemical change is often open to doubts.

Nitric acid is again a good example to illustrate the limits of interpretation. Various properties of nitric acid solutions indicate that the molecular constitution is essentially different above and below the composition of the monohydrate $\text{HNO}_3 \cdot \text{H}_2\text{O}$. Raman spectra show that the concentration of ions is very low in the upper range. Dalmon and Freymann²⁹ demonstrated beyond any doubt that nitric acid in this range is associated. Since carboxylic acids are known to associate only to dimers and the hydrogen bonding situation is the same, it is very likely that nitric acid, too, forms dimers rather than higher associates. Addition of water to nearly anhydrous acid therefore can be approximately described by the reaction



Ionization ensues, roughly speaking, as soon as this reaction is completed, i.e., on dilution below $\text{HNO}_3 \cdot \text{H}_2\text{O}$. This fact, by the way, shows that more water must be bound to the ions than only the one molecule in the hydronium

ion. Chédin's³⁰ thorough discussion of the molecular state of nitric acid in the whole concentration range undoubtedly furnishes a correct description of the essential features, though the details and numerical results may be considered to be not finally established.

Dimerization above, and dissociation below, the equimolal concentration is equally clearly indicated in the n.m.r. of aqueous solutions of trifluoroacetic²⁵ and heptafluorobutyric²⁶ acids. Some essential features of Hantzsch's early suggestions concerning the molecular constitution of acids are surprisingly well confirmed.

The molecular constitution of anhydrous nitric acid unquestionably has been brilliantly elucidated by the discovery of the nitronium ion. The thorough cryoscopic investigation by Gillespie, Hughes and Ingold³¹ and the measurement of conductivities by Lee and Millen³² have contributed a wealth of reliable information. Yet not all detailed quantitative interpretations appear to be safely established.

Essentially, quantitative conclusions were based on the assumption that the solutions investigated are ideal dilute solutions. An influence of ionic interaction was not observed and was believed to be negligible because the dielectric constant of the solvent is unquestionably very high.

In a problem of this nature we have to distinguish between effects of first and second order. As far as first-order effects go, the assumption of an ideal dilute solution leads to the numbers of dissolved molecules or ions per molecule of added solute. Often this information is sufficient for establishing the nature of the molecular species in the solution, except for solvation numbers. There cannot be any doubt that the experimental results of Gillespie *et al.* establish the validity of their conclusions as far as first-order effects are concerned.

In a development of the thermodynamic properties of a solution into a power series with respect to the concentration, the molal weight of the solvent (or the number of moles per kilogram of solvent) is not involved in the first-order term. It does appear, however, in the terms of higher order. Solvation numbers, according to the correctly derived relations of Gillespie *et al.*, depend on second-order effects. They also depend on the assumed molal weight of nitric acid. Gillespie *et al.*, assuming monomeric nitric acid, found that water is solvated with 2HNO_3 , the ions formed by N_2O_5 with 4HNO_3 . On the basis of dimeric nitric acid, the solvation numbers 2.5 and 5, respectively, are obtained. Still higher values result if higher association of the acid is assumed. Quite apart from these uncertainties, the solvation numbers cannot be relied upon. The validity of the laws of the dilute solution as limiting laws has been established. But this fact does not in any way support the assumption that the deviations found with increasing concentration are due to solvation rather than ionic or molecular interaction.

The degree of self-dissociation is given essentially by the difference between the maximum at the composition HNO_3 in the freezing curve of the system $\text{H}_2\text{O} + \text{N}_2\text{O}_5$, and the peak obtained by extrapolation of the freezing curves to the left and right of the maximum. This is a first-order effect, independent of the molecular structure of the solvent, and therefore in principle well established by the results of Gillespie *et al.*, though the extrapolation can hardly be very accurate.

In the derivation of the degree of self-dissociation from conductivities, Lee and Millen³² introduced an equilibrium constant expressed in mole fractions, basing the calculation on the molecular size HNO_3 (24.825 mole/l. at -10°C). Actually the influence of self-dissociation on the conductivity is again a first-order effect and as such essentially independent of the molecular structure of the solvent. To show this, one has to change the calculation of Lee and Millen only in minor points.

The derivation is based on the constancy of the equilibrium constant of the self-dissociation

$$K_a = a(\text{NO}_2^+) \cdot a(\text{NO}_3^-) \cdot a(\text{H}_2\text{O})/[a(\text{HNO}_3)]^2. \quad (2)$$

The activities of NO_2^+ and NO_3^- are approximated by the concentrations, which are given by the measured specific conductivity κ and the molal conductivity Λ according to

$$a(\text{NO}_2^+) = a(\text{NO}_3^-) = 1000\kappa/\Lambda. \quad (3)$$

The activity of H_2O is approximated by the concentration of $\text{HNO}_3 \cdot \text{H}_2\text{O}$, which is equal to that of NO_2^+ or NO_3^- in the pure acid but larger by the concentration of added H_2O and smaller by the concentration c of added N_2O_5 since this addition contributed to NO_2^+ and NO_3^- but not to $\text{HNO}_3 \cdot \text{H}_2\text{O}$. We count added water as negatively added N_2O_5 and approximate

$$a(\text{H}_2\text{O}) = 1000\kappa/\Lambda - c. \quad (4)$$

The activity of the solvent HNO_3 is assumed to be constant.

With these approximations, eqn. (2) becomes

$$K = (1000\kappa/\Lambda)^2(1000\kappa/\Lambda - c). \quad (5)$$

The conductivities κ observed by Lee and Millen as a function of the concentration c at -10.02°C can be represented with a practically constant value of Λ , namely, $\Lambda = 66 \pm 1$. In order to check this result, one introduces the estimate $\Lambda_0 = 66$ for $c = 0$, $\kappa = \kappa_0$, and divides (5) by

$$K = (1000\kappa_0/\Lambda_0)^3 \quad (6)$$

to obtain

$$(\Lambda/\Lambda_0)^3 = (\kappa/\kappa_0)^3(1 - c\Lambda/1000\kappa). \quad (7)$$

This equation is solved by successive approximation. For high values of c one has to invert eqn. (7).

There is no essential reason for a preference of either the present value $\Lambda = 66$ or the value $\Lambda = 71.9$ of Lee and Millen. Both are subject to the inherent uncertainties of first-order calculations applied to fairly high concentrations. But calculations of higher order are in principle unjustified, in view of the second-order uncertainties concerning the molecular size of the solvent and the influence of ionic interaction on equilibrium and conductivity.

The investigations of Gillespie *et al.*, and Lee and Millen have been chosen as an illustrative example because there is nothing unclear or vague in their presentation so that we have the advantage of a simple discussion of a simple matter. Moreover, their work contains extremely valuable information so that a clean limitation of the conclusions appeared to be desirable.

The scope of the present discussion, however, is not restricted to the over-extended use of the model of the dilute solution. Whether the limiting law is that of the dilute solution or of Debye and Hückel or any other, we are justified in interpreting deviations as chemical changes only on the basis of specific additional evidence, never because an added arbitrary "equilibrium constant" removes the first deviation from the limiting law.

It is at this point that one runs, even nowadays, across the objection: even if the assumption of a chemical change as distinguished from physical interaction is not finally corroborated, it serves for the representation of observations. Up to this day we have not noticed any advantage of this interpretation. But it is clear what we lose: the clear border line between real chemical changes, safely established by Raman spectra or otherwise, and the ordinary, always present interaction.

CONCLUSIONS

The dissociation of electrolytes expresses itself, of course, in the variation of many properties with the concentration. Not only activity coefficients and heat contents but also the molal volume³³ are influenced in a characteristic and unmistakable fashion. Refractivity, on which we owe so much to Fajans, and even Verdet's effect³⁴ reflect the influence of dissociation. But none of these properties, taken by itself, provides a *primary* method for the quantitative description of dissociation. They cannot because they are colligative rather than specific and, more important, they are too much influenced by the environment of the molecule

or ion. Electrical conductivity and light absorption are specific but they, too, are too much subject to environmental influences. Whenever a quantitative method is based on one of these properties, some assumptions inevitably must be introduced for which we have no internal test.

The situation, however, has changed now in that an external test can be provided. In other words, some properties may serve as a basis for secondary methods after the inevitable assumptions have been checked with the aid of the few acids which have been sufficiently well examined. These acids can be used as calibration samples for the check of the usefulness of various methods.

Our discussion of nuclear magnetic resonance essentially involves such a check. Similar comparisons involving results obtained by other methods would contribute greatly to an extension of the basis of safe information on dissociation.

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