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The Ionization of Strong Electrolytes. I. General Remarks, Nitric Acid

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The problem of the ionization of strong electrolytes, discussed from various viewpoints during more than fifty years, is complicated by the fact that some uncertainty exists regarding the use of the terms ionized and undissociated. In an early period the idea has already been expressed that "interionic attraction" and "formation of molecules" are just two equivalent terms. Bjerrum[2] by no means endorsed this idea, when he successfully introduced the concept of "ion pairs" as a useful model for an approximate calculation of electrostatic interaction between ions at moderate concentrations. Later use of this concept, however, sometimes raises doubt as to the border line between ion pairs and molecules. The inherent difficulty is made manifest by a recent discussion of Fajans and Johnson,[3] who point out that any kind of intermediate forms between ionic and covalent bonds may exist, and consider ion pairs and molecules to correspond to the two bond types.

Obviously an experimental criterion is required which distinguishes between molecules (or intermediate ions) and the dissociation products on cogent theoretical grounds. The vibration spectrum represents a criterion of this kind.

Two ions possess six translational degrees of freedom, a molecule only three. In the formation of a molecule, at least one of the three lost translational modes is transformed into a vibration (the other two change either to vibrations or rotations). In any case, the vibration spectrum of a molecule must be definitely different from the spectrum of the two ions.

The Raman spectrum, while not always furnishing the complete vibration spectrum, is in general sufficient for a safe answer. In each special case the change to be expected for the formation of a molecule must be discussed with regard to the general theory of vibrations and the selection rules of Placzek.

Probably the only case in which the Raman spectrum does not present an unambiguous decision is that of diatomic electrolytes the ions of which do not show any vibrations. The fact that no Raman line of sodium chloride in aqueous solution has been discovered, must not be taken as definite evidence of complete dissociation. Indeed, owing to the polar character of the bond, the intensity of the line of an Na-Cl vibration might well be below the sensitivity of the experiment. In this case, recourse should be made to infrared spectra.

Border-line cases in which the lifetime of a molecule is comparable with a vibration period, between 10^{-14} and 10^{-12} seconds, will be characterized by an anomalous line width. Actually the width of the lines of the undissociated molecules of nitric and perchloric acids is abnormally large, but this can also be ascribed to other causes like influence of the environment.

Of course, the whole array of Raman data furnishes experimental evidence of the one-to-one correlation of molecules or ions and their vibration spectra. Since the Raman spectrum of concentrated nitric acid has been interpreted as a superposition of the spectra of the ion and the molecule,[4] ample evidence of the characteristic nature of the spectra of the ions and the undissociated molecules of electrolytes has been recorded. Characteristic spectra have been found also of complex ions.[5]

The Raman spectrum unambiguously distinguishes between formation of molecules and ionic interaction. The former is characterized by new lines *in addition* to the lines of the ions, the latter often causes a gradual change of the frequency with the concentration. The magnitude of this change is, in general, a characteristic property of the interacting ions, reflecting the specific nature of ionic interaction as stressed by experimental results and theoretical discussions of Brönsted, Bjerrum, Fajans and other authors.

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(2) N. Bjerrum, *Mat.-Fys. Medd. Kgl. Dansk. Vid. Selsk.*, **7**, no. 9 (1926); *Ergeb. exakt. Naturw.*, vol. 5, Berlin 1926, p. 125.

(3) K. Fajans and O. Johnson, *Trans. Am. Electrochem. Soc.* (1942). We are indebted to Professor Fajans for the privilege of reading the manuscript. See also K. Fajans, H. Kobner and W. Geffcken, *Z. Elektrochem.*, **34**, 1 (1934).

(4) (a) I. R. Rao, *Proc. Roy. Soc.* (London), **A127**, 279 (1930), or *Proc. Roy. Soc.* (Amsterdam), **33**, 632 (1930); (b) E. L. Kinsey and J. W. Ellis, *Phys. Rev.*, **35**, 284 (1930); (c) E. L. Kinsey and J. W. Ellis, *Phys. Rev.*, **36**, 603 (1930); (d) L. A. Woodward, *Phys. Z.*, **32**, 212 (1931); (e) R. Brunetti and Z. Ollano, *Nuovo cimento*, N.S. **8**, 189; *Atti Accad. Lincei*, **13**, 52 (1931).

(5) O. Redlich, T. Kurz and P. Rosenfeld, *Z. physik. Chem.*, **B19**, 231 (1932), and later papers of several authors.

The distinction between the ions and the undissociated molecule by means of the vibration spectrum does not touch the question of the nature of the bond.

The Raman spectra of alkali nitrate solutions of any concentration contain only the lines of the nitrate ion. In addition, the intensity of these lines is proportional to the concentration. Alkali nitrates, therefore, are completely dissociated. "Ion pairs," undoubtedly present in concentrated alkali nitrate solutions, are not molecules. Many uni-di-valent electrolytes, however, appear to be incompletely ionized.[6]

Degrees of Ionization Derived from Raman Spectra

I. R. Rao,[4a] Simons[7] and Chédin[8] compared the intensities of the nitrate ion line 1048 cm.$^{-1}$ in the spectra of nitric acid solutions of various concentrations. The assumption that the intensity of a Raman line is *proportional* to the concentration of the exciting substance is in accord with whatever is known on the relationship between these two quantities. However, the assumptions tentatively used by the three authors in order to determine the degrees of ionization themselves are at variance with the modern theory of electrolytes.

A thermodynamic method was proposed[9] to derive the ionization constant and the degrees of ionization from the results of the earlier authors. However, while the method is believed to be correct, its extreme sensitivity to experimental errors was pointed out. Therefore, the results ($K = 1.9$, 1.2 and 24 from the data of Rao, Simons and Chédin, respectively) were not expected to be more than very rough estimates.

At the same time, however, a new method was suggested[9a] which promised to furnish reliable results. It consists in comparing the intensity of a nitrate ion line, obtained in the spectrum of a *nitric acid* solution, with the intensity of the same line, obtained from a *sodium nitrate* solution. Thus the unknown factor connecting the intensity of the line and the true ionic concentration is eliminated by direct experiment.

While the present work was in progress, N. R. Rao[10] published results obtained by the same method, apparently without knowledge of the earlier discussion.[8] Meanwhile we had supplemented and modified the procedure.

First, in the range between 10.3 and 14.2 moles per liter, the intensities of the lines 1301 and 926 cm.$^{-1}$ of the *undissociated* molecule were compared. Second, in the range below 10.3, each nitric acid solution was compared with at least two suitably chosen sodium nitrate solutions so that the intensity of the nitrate line 1048 cm.$^{-1}$ of the acid was between the values of the salt solutions. Thus the measurement constitutes a direct empirical interpolation, practically a comparison of two lines of equal intensity. The difficulties involved in a comparison of lines of unequal intensity are avoided.

Experimental Details

A Gaertner spectrograph similar to L256, but with a camera lens of 500 mm. focal length, was used. The light source was a water-cooled mercury arc operating at 8 or 9 amp. and about 70 volts. Exposure times ran from one minute to about one hour, depending on the speed of the plate, slit width, concentration, etc.

Solutions were sealed in Pyrex cells of 22 mm. o.d. and 200 mm. illuminated length. The cells of the earlier runs were provided with blown windows, those of the later runs with sealed-on ground and polished windows. In a test run with sulfuric acid in twelve cells of the latter kind the maximum deviation of the intensity of a suitably chosen line from the average was 7%. Two cells with larger deviations were discarded.

In the earlier runs the light was concentrated on the slit in the usual way. Later the condenser and cell were adjusted so that all light passing the slit hit the collimator lens and small differences in the position of the cell were harmless.

In the comparison of lines of the undissociated acid a step-filter was used prepared by exposing a photographic film.[11]

The exposure times of a run were equal and all exposures were taken on one plate. Each run included the necessary comparison spectra and therefore furnished an independent experimental result.

Small fluctuations of the apparent arc resistance were compensated so that the arc wattage was constant. In a test run with exposures at 8, 9 and 9.5 amp. the intensities were 0.93:1:1.02. As the fluctuations usually amounted to not more than ±0.2 amp., the resulting error was negligible.[11a]

For the early runs a microphotometer constructed by Dr. S. T. Stephenson was used; later the tracings were taken by means of a Zeiss instrument.[12]

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[6] This question will be discussed in a later paper of this series.

[7] L. Simons, *Soc. Sci. Fenn. Comm. Phys. Math.* (VI1) 1933, No. 9.

[8] J. Chédin, *Ann. Chim.*, [11] **8**, 243 (1937).

[9] (a) O. Redlich and P. Rosenfeld, *Sitz. Ber. Akad. Wiss. Wien*, 11b, **145**, 87 (1936) or *Monatsh.*, **67**, 223 (1936); (b) O. Redlich, *Z physik. Chem.*, **A182**, 42 (1938).

[10] N. R. Rao, (a) *Indian J. Phys.*, **14**, 143 (1940) (H_2SO_4); (b) **15**, 185 (1941) (HNO_3).

[11] We are indebted to Dr. D. Lipkin for this stepfilter.

[11a] A considerable part of the extensive tests of the experimental method has been carried out by Mr. E. K. Holt.

[12] The authors express their thanks to Professor S. T. Stephenson, Pullman, and Professor R. T. Birge, Berkeley, for the use of these instruments.

One source of error, mentioned also by N. R. Rao, could not be eliminated to the desired extent, namely, the influence of the unequal width of the spectral lines. It is well known that the opacity of the photographic plate is far from being proportional to the intensity of the incident light. Two spectral lines of equal total intensity but of different width therefore produce microphotometer curves which are different not only with respect to the height but also to the area beneath the curve. Moreover, the ratio of the areas varies widely with the intensity. This effect was conspicuous on several plates on which the nitrate lines excited by both the blue and the violet mercury lines were used for a comparison of the nitrate ion concentration of two solutions. Sometimes the two intensity ratios were even reverse to each other.

The effect is complicated by the fact that the intensity curve is influenced by several factors, namely, the width of the spectrograph slit, the curvature of the lines, and the width of the microphotometer slit. A stepwise elimination of these factors and a systematic analysis of the line width effect appear to be hardly feasible.

An attempt was made to eliminate the line width effect by the use of a wide spectrograph slit. As soon as the slit width is large compared with the natural width of the line, the line width should be insignificant and both the height and the area of the curve should represent sufficiently true measures of the intensities. A systematic study, however, in which the spectrograph slit was widened up to 1.6 mm., revealed that the nitrate line of nitric acid solutions was appreciably affected by the near line of the undissociated molecule.

As the difference between the results derived from the lines excited by the blue and violet mercury lines was the most conspicuous symptom of the line width effect, it was assumed that the error was small whenever the two lines furnished concordant results in the same run. Since the intensities of the two lines are appreciably different, concordant results indicate that all lines were for the main part in regions where the opacity is an approximately linear function of the intensity. This criterion was strictly adopted for the comparison of nitric acid and sodium nitrate solutions in which the effect is most important. A considerable number of runs were rejected, in which the intensities of the violet lines either were not measured or furnished a nitrate ion concentration which deviated more than 0.4 mole per liter from the result of the blue lines. While we believe that this selection had to be made for *a priori* reasons, the final average result was not appreciably changed by it. Measurements were made at room temperature, *i. e.*, 24 to 28°.

Results

The results obtained by direct comparison of the nitrate line 1048 cm.$^{-1}$ in nitric acid and sodium nitrate solutions are given in Table I, where c denotes the analytical concentration of nitric acid in moles per liter, and αc the true concentration of the nitrate ion. Excitation of the nitrate line by the blue and violet mercury line is denoted by b and v, respectively.

Table II contains the results for the concentration of the undissociated molecule obtained by comparison with an acid with 10.30 moles per liter. The figures are based on the assumption that the nitrate ion concentration of this acid is αc = 4.03.

TABLE I

CONCENTRATION OF THE NITRATE ION

$c \rightarrow$	4·51		6·60		8·90		10·30	
	b	v	b	v	b	v	b	v
αc	3.61	3.50	4.27	4.28	4.27	4.39	3.77	3.69
	3.87	3.78	4.27	4.56	4.27	4.43	4.39	4.09
	3.79	3.71	4.25	4.06	4.42	4.13	4.13	4.10
	3.86	3.56	4.49	4.48				
			4.15	4.08				
			4.89	4.68				
Av.	3.78	3.64	4.46	4.43	4.39	4.32	4.10	3.96

TABLE II

CONCENTRATION OF THE UNDISSOCIATED MOLECULES

c	11·89	14·23
$(1 - \alpha)c$	8.3	12.1
	7.8	12.1
	8.4	12.0
	7.9	12.0
		9.4
		12.9
		11.8
		14.9
		12.5
Average	8.1	12.2

These results, together with the data of earlier observers and of N. R. Rao, are represented in Fig. 1. Rao's results are close to our curve. The figures derived previously by one of the authors[9b] from the experimental results of Chédin[8] and von Halban and Eisenbrand[13] agree as well with the present results as could be expected.

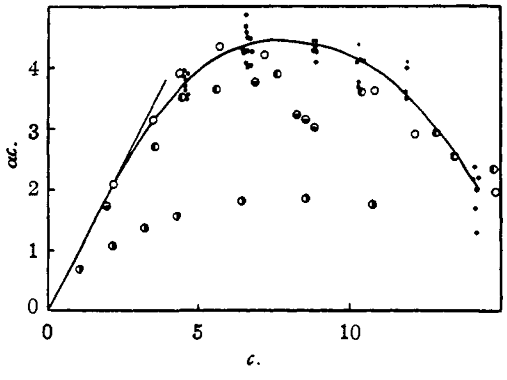

Fig. 1.—Dependence of the concentration of the ions αc on the total concentration c: ◑, data of Simons calculated by Redlich and Rosenfeld; ◐, data of Chédin calculated by Redlich; ⊖, data of Halban and Eisenbrand calculated by Redlich; ○, N. R. Rao; •, this paper. The straight line indicates complete ionization.

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[13] H. von Halban and J. Eisenbrand, *Z. physik. Chem.*, **132**, 433 (1928).

The data of Tables I and II furnish a fairly reliable basis for a determination of the dissociation constant

$$K = a_2/(1 - \alpha)\beta c \qquad (1)$$

where a_2 denotes the activity referred to the conventional standard state, and β the "true" activity coefficient, *i. e.*, the activity of the undissociated molecules is represented by $(1 - \alpha)\beta c$ with $\beta = 1$ for $c = 0$.

According to equation (1) the values of $K\beta$ can be calculated from experimental data. Extrapolation of $K\beta$ to $c = 0$ furnishes K. Theory[14] and experimental data[15] indicate linear dependence of log β on the ionic concentration in dilute solutions. The extrapolation is therefore carried out in log $K\beta$.

The activities of concentrated nitric acid solutions can be derived only from measurements of the partial vapor pressures. As recently pointed out by Forsythe and Giauque,[16] the inconsistency of these data with the Duhem–Margules equation indicates considerable errors in at least part of them. In view of this inconsistency we have chosen[17] what we considered "best values" by assuming that the relative error is highest for low partial pressures.[18] For the present purpose of extrapolation the uncertainty of the activity coefficients is believed to be of minor importance. Table III contains the values of a_2/c (calculated from ref. 17) and the average of $1 - \alpha$, as used in computing $K\beta$.

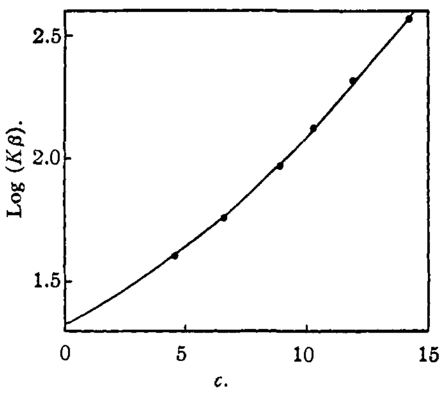

Fig. 2.—Diagram of log $K\beta$ = log $a_2/(1 - \alpha)c$, calculated from the average values of Tables I and II, against concentration.

TABLE III

c	4.51	6.60	8.90	10.30	11.89	14.23
m	5.20	8.25	12.41	15.79	20.1	28.8
a_2/c	7.21	18.8	47.3	81	140	322
$1 - \alpha$	0.177	0.327	0.51	0.61	0.68	0.86

The extrapolation of log $K\beta$ (*cf.* Fig. 2) yields $K = 21 \pm 4$, where the limits of error represent a rough estimate.

Conclusions

Only a few crude and by no means reliable estimates of the order of magnitude can be compared with the present result $K = 21$.

The close agreement of the value $K = 24$, derived by one of the authors[9b] from Chédin's data,[8] is entirely fortuitous. Wynne-Jones[19] estimated $K = 14$, extrapolating by means of Born's equation the ionization constants of nitric acid in nonaqueous solutions. This agreement, too, must be considered somewhat fortuitous as Born's equation is not always successful in describing the dependence of the free energy on the dielectric constant if various solvents are involved.[20] Kossiakoff and Harker[21] estimated ionization constants on the basis of reasonable assumptions concerning the structure and the mechanism of ionization. Their value, log K = 0.1, is in sufficient agreement with our results. Also the agreement with the value $K = 9$, derived[9b] from the ultraviolet extinction coefficients of von Halban and Eisenbrand,[13] is satisfactory. Our result coincides with the lower limit derived by von Halban and Seiler[22] from measurement of the light absorption of an indicator.

Hantzsch[23] describes the equilibrium between the supposed *aci*- and the *pseudo*-form by means of a curve derived from ultraviolet extinction coefficients. This curve corresponds in a roughly qualitative way to the ionization equilibrium though the differences are very large. The as-

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(14) P. Debye and J. MacAuley, *Physik. Z.*, **26**, 22 (1925).

(15) *Cf.* M. Randall and C. F. Failey, *Chem. Rev.*, **4**, 271, 285, 291 (1927).

(16) W. R. Forsythe and W. F. Giauque, THIS JOURNAL, **64**, 48 (1942).

(17) O. Redlich and P. Rosenfeld, "Activity Coefficients" in Landolt–Börnstein, "Physikalisch-chemische Tabellen," 5th edition, 2nd and 3rd supplement, J. Springer, Berlin, 1931 and 1936. For just the same reason, precise determinations of the freezing points were extended to a molality as high as 6.6 *M* (−34°); *cf.* E. Abel, O. Redlich and B. v. Lengyel, *Z. physik. Chem.*, **132**, 189 (1928); F. Hartmann and P. Rosenfeld, *ibid.*, **A164**, 377 (1933).

(18) The decomposition of nitric acid, probably one of the major sources of error at higher concentrations, could be prevented by means of ozone. The appearance of nitrogen pentoxide in the vapor over anhydrous or nearly anhydrous acid constitutes another possible source of error.

(19) W. F. K. Wynne-Jones, *J. Chem. Soc.*, 1064 (1930).

(20) For references see O. Redlich and J. Bigeleisen, *Chem. Rev.*, **30**, 171 (1942).

(21) A. Kossiakoff and D. Harker, THIS JOURNAL, **60**, 2047 (1938).

(22) H. von Halban and M. Seiler, *Z. physik. Chem.*, **A181**, 70 (1938).

(23) A. Hantzsch, *Ber.*, **58**, 941 (1925).

sumption of an *aci*-form is based entirely on methods of the classical theory of electrolytes and therefore without any real basis.

The "intermediate" form of von Halban and Eisenbrand[13] is identical with the undissociated molecule. The difference between the absorption spectra of the molecule in aqueous solution and in hexane, which led to the assumption of a second form, must be explained by strong interaction between the molecules; the assumption of a hydrogen bond is, of course, very obvious. Indeed, Dalmon and Freymann[24] by determining the infrared absorption at the frequency of the hydrogen vibration furnished definite evidence of the formation of a hydrogen bond in the range between 80 and 100% HNO_3, *i. e.*, in the range where less than one water molecule is available per molecule of the acid. Another factor interfering with the interpretation of ultraviolet spectra, the presence of nitrogen pentoxide in anhydrous acid, is supported by the Raman spectra of Susz and Briner and of Chédin.

These difficulties, encountered in the derivation of degrees of ionization from extinction coefficients have been pointed out by von Halban and Eisenbrand. Nevertheless, considering the satisfactory agreement shown in Fig. 1, and the success of Fromherz' measurements[25] on moderately strong electrolytes, more information can be expected from this source.

From Fig. 1 one must expect that the concentration of the ions is already very low at 18 moles of HNO_3 per liter, corresponding to the composition $HNO_3 \cdot H_2O$. Association by hydrogen bonds and formation of nitrogen pentoxide explain the surprisingly quick decrease of the ionization with increasing concentration.

The rapid increase of the partial molal heat contents[26] of nitric acid above $c = 3$ corresponds to the decrease of the ionization as indicated by Fig. 1. We intend to discuss the thermodynamic properties on a later occasion.

The authors wish to thank Professor G. N. Lewis for illuminating discussions.

Summary

1. A characteristic Raman spectrum represents a sufficient and under certain conditions necessary criterion of the existence of undissociated molecules and intermediate or complex ions.

2. According to this criterion, alkali nitrates and a number of other uni-univalent salts are completely ionized. Ion pairs are not to be classified as undissociated molecules.

3. The degrees of ionization of nitric acid have been determined by a method previously suggested.

4. The thermodynamic ionization constant of nitric acid is $K = 21$. Earlier crude estimates of the order of magnitude of the ionization constant are compared with the present result.

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[24] R. Dalmon and R. Freymann, *Compt. rend.*, **211**, 472 (1940).

[25] H. Fromherz and Kun Hou Lih, *Z. physik. Chem.*, **A153**, 321 (1931); H. Fromherz, *ibid.*, **153**, 376 (1931). *Cf.* also E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

[26] *Cf.* the values calculated (ref. 9a) from the data of G. Becker and W. A. Roth, *Z. physik. Chem.*, **A174**, 104 (1935).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN]

The Preparation and Properties of Potassium Thiogermanate and Thiogermanic Acid[1]

BY HOBART H. WILLARD AND C. W. ZUEHLKE

Germanium sulfide may be classified among the least soluble sulfides, it being quantitatively precipitated from solutions 6 *N* in hydrogen ion concentration. In 1886 Winkler[2] showed that germanium sulfide is not precipitated, however, from weakly acid solutions and he postulated the existence of a stable thiogermanate as an explanation of this behavior. Abrahams and Müller[3] utilized this property as the basis of a separation of arsenic from germanium. They showed that arsenic is quantitatively precipitated as the sulfide from a solution which is less than 0.09 *N* in hydrogen ion concentration, while germanium remains in solution under these conditions. Schwarz and Giese,[4] noting the solubility of germanium sulfide in alkali sulfides, isolated $Na_6Ge_2S_7$ and $K_6Ge_2S_7$

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[1] From a dissertation submitted by C. W. Zuehlke to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Winkler, *J. prakt. Chem.*, [2] **34**, 220 (1886).

[3] Abrahams and Müller, THIS JOURNAL, **54**, 86 (1932).

[4] Schwarz and Giese, *Ber.*, **63**, 779 (1930).