SYMPOSIUM ON THERMODYNAMICS AND MOLECULAR STRUCTURE OF SOLUTIONS[1]

Introductory Remarks

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Received October 25, 1948

The problem of the relationship between the thermodynamic properties and the molecular structure of solutions has run through the full zigzag course which is the usual fate of a theory. The early successes of the laws of the dilute solution led to the extreme of Dolezalek's theory (10), according to which all solutions are perfect and all apparent deviations from the laws of the perfect solution are due to association of the components and to the formation of compounds.

As fashions go, the reaction came in the 1920's, under the impact of the theory of Debye and Hückel. While Dolezalek completely disregarded intermolecular and interionic forces, there appeared now a tendency to forget entirely the possible existence of chemical bonds and undissociated or associated molecules.

Actually, neither of the extreme tendencies was ever fully adopted though their influence at times was quite strong. But the proper middle course led to a difficult question: How can we give both ionic or molecular interaction and chemical bonds their due shares? Many properties, for instance, the heat of mixing, do not present a safe criterion. In extreme cases, of course, the distinction is obvious. The heat of mixing of sulfuric acid and water is undoubtedly a heat of reaction, while the heat absorbed on diluting a solution of sodium nitrate is due to interionic forces. But the heat content does not indicate a clear border line, nor does any other thermodynamic property. The same is true for other properties such as the refractivity or the viscosity.

Nevertheless a fairly clear-cut distinction, based directly on the traditional concept of the molecule, can be made. Any dissociation or association changes the number of vibrational frequencies. As soon as the vibration spectrum is fully known and interpreted, no doubt is left regarding the molecular state of a solution. But often a full knowledge of the vibrations is not necessary. A frequently discussed criterion is this: If in a solution the frequency of a Raman line or an infrared band continuously changes on changing the concentration, the shift is due to interaction with the environment. If one line gradually becomes less intense and a different line appears and becomes stronger, we may safely assume an equilibrium between two molecular species.

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[1] Presented at the Symposium on Thermodynamics and Molecular Structure of Solutions, which was held under the auspices of the Division of Physical and Inorganic Chemistry at the 114th Meeting of the American Chemical Society, Portland, Oregon, September 13 and 14, 1948.

For an illustration of the use of vibration spectra and other properties in the elucidation of the molecular state, I should like to discuss a few examples which have found no other place on the program of this symposium.

The molecular state of nitric acid has been the subject of many investigations for a long time. Twenty years ago Hantzsch (15, 16) tried to support his theory of pseudo acids by a discussion of nitric acid, and Halban and Eisenbrand (14) encountered some difficulties in the interpretation of their careful measurements of the ultraviolet spectrum. Since that time numerous authors have contributed considerable information on the molecular state of nitric acid. Only the two latest results will be discussed here. One refers to aqueous nitric acid in the range between 80 and 100 weight per cent, the other to the range above 94 per cent and to mixtures with sulfuric acid.

According to Dalmon and Freymann (9) and to Chédin and Fénéant (5), the hydrogen band observed in the infrared and Raman spectra of aqueous nitric acid solutions undergoes a considerable change in the range between 80 and 100 per cent. The most intensive component in anhydrous nitric acid is found at 3400 cm.$^{-1}$ It gradually disappears on dilution to 80 per cent, while another intensive component at 3560 cm.$^{-1}$ and several weaker and lower frequencies appear. In the same range the deformation vibration, 608 cm.$^{-1}$, is gradually replaced by 637 cm.$^{-1}$ (5). These changes have nothing to do with ionization, since nitric acid is very little ionized in this whole range. The qualitative explanation is obvious. Anhydrous nitric acid is associated through hydrogen bonds. On addition of water, these bonds are replaced by hydrogen bonds between nitric acid and water. This process is complete at 80 per cent, which corresponds to the composition of the monohydrate. On further addition of water, ionization increases rapidly. There are various possibilities for hydrogen bonds between nitric acid molecules and between the acid and water. The available data do not appear to be sufficient for a detailed description.

For a long time it has been assumed that nitric acid in aqueous solution between 94 and 100 per cent and in mixtures with concentrated sulfuric acid is slightly decomposed into nitrogen pentoxide and water. Recently Westheimer and Kharasch (23), Bennett, Brand, and Williams (1), and Ingold and his coworkers (13, 17) have shown that a dissociation actually takes place but that it leads to a positive ion, the nitronium ion:

$$3HNO_3 = NO_2^+ + NO_3^- + HNO_3 \cdot H_2O$$
$$HNO_3 + 2H_2SO_4 = NO_2^+ + 2HSO_4^- + H_3O^+$$

The evidence is overwhelming. It includes extensive earlier experimental results of Chédin and his coworkers (4, 5, 12). A Raman line at 1394 cm.$^{-1}$ is now satisfactorily explained as due to the linear NO_2^+ ion. The freezing-point depression in sulfuric acid is in accord with the electrolytic dissociation furnishing four ions per mole of nitric acid. The absence of nitric acid lines in the Raman spectrum of solutions in sulfuric acid containing less than 15 mole per cent nitric acid and the negligible partial pressure of nitric acid over these solutions furnish further evidence. The most direct proof, however, is presented by the cathodic migration of nitrogen in sulfuric acid solutions.

Very impressive is also the influence of the nitronium equilibrium on the heat content (7). Solutions containing a little less water than corresponds to HNO_3, i.e., nominally 101 per cent HNO_3, liberate only a few hundred calories per mole of water on dilution. The heat evolution increases very rapidly and attains a maximum of 4100 cal. per mole of water at 97 per cent. On further dilution the heat effect decreases steadily. This means, of course, that the combination of nitronium ion, nitrate ion, and water to nitric acid absorbs heat, while a large amount of heat is produced by the depolymerization of the acid.

Chédin and his coworkers (4, 6) have shown, especially by the examination of Raman spectra and vapor pressures, that the molecular state of nitric acid in mixtures with sulfuric acid and water can be described in a fairly quantitative way.

The conclusions for the kinetics of nitration are obvious and well established (23): rapid nitration in anhydrous nitric acid or in mixed acid is due to the nitronium ion.

As another example I should like to discuss briefly the problem of the association of water. The basic hypothesis, that ice molecules are present in liquid water at low temperatures, was proposed by Whiting in 1884 and elaborated by Roentgen in 1892. This hypothesis was in various ways expanded by numerous authors (for earlier references see 3 and 22). The mechanism of the association was explained by Latimer and Rodebush (20) when they pointed out the existence of hydrogen bonds. The essential points of the earlier hypothesis were confirmed and elucidated by Bernal and Fowler (2; see also 21) in 1933. These authors, indeed, found by means of x-ray analysis that in cold water the structure of ice persists over short ranges (each water molecule is tetrahedrally surrounded by four molecules at a distance of 2.76 Å.). This structure disappears gradually on heating.

Qualitatively the picture is quite clear. Various numbers of water molecules are connected by hydrogen bonds to associated molecules. The equilibrium is, of course, dynamic and the life of an associative bond probably short. The larger aggregates enclose an appreciable amount of hollow space to produce the abnormally large volume of cold water. The influence of temperature, pressure, and solutes in breaking down the associated molecules is in accord with thermodynamic principles. This model explains qualitatively all the perplexing properties of water,—volume, expansibility, compressibility, specific heat, infrared and Raman spectra, viscosity, and so on.

Regarding quantitative information, we should like to know the properties and concentration of each molecular species or at least of the associative bonds. Actually our quantitative knowledge is extremely scanty. The simplest assumption would be that of a continuous association as proposed by Lassettre (19) and by Kempter and Mecke (18) for other hydroxyl compounds. But according to the results of Cross, Burnham, and Leighton (8) and of Eucken (11) it may be questioned whether continuous association represents a very good approximation. It is quite possible that some polymers, for instance $(H_2O)_8$ (11), are favored. At low temperatures there is undoubtedly a considerable amount of aggregate of higher than fourth order present, since polymers of lower order cannot enclose an appreciable hollow space. On the other hand, association to very much larger molecules is not likely because then we would have to expect a high viscosity. It was pointed out (22) in 1929 that no basis for definite statements regarding the size of the associated molecules is available. This situation has undergone little change.

Somewhat more definite is our knowledge of the heat of association. From a discussion of the Raman spectrum Cross, Burnham, and Leighton (8) derived a crude estimate of 3 kcal. for the heat of formation of a hydrogen bond. Eucken (11), on the other hand, obtained the heat of association for various polymers from the specific heat. His estimates, changed to the heat of formation of one bond, are reasonably close to 3 kcal.

Some time ago an attempt was made (22) to derive the temperature dependence of the concentration of the higher polymers from the intensity of infrared absorption. The result is in good agreement with a recent estimate of Eucken (11), based on the specific heat and the volume.

The average number of hydrogen bonds per formula weight is estimated by Cross, Burnham, and Leighton to be slightly higher than two at 26°C., according to the intensity of Raman bands.

These are meager results. But there is no reason to doubt that the quantitative description of the association equilibrium of water presents a significant and solvable problem.

Twenty years ago, when various attempts to extend the theory of Debye and Hückel to concentrated solutions were not very successful, a certain pessimism was the natural consequence. The examples discussed here indicate that the molecular theory of solutions need not be restricted to the state of high dilution.

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