

SOME CONSIDERATIONS ON HYDRATION AND SOLUTION¹

BY H. AUSTIN TAYLOR

Since the time when the properties of solutions were regarded as being caused by general hydration, as an alternative to the ionic theory, chemical literature has been inundated at intervals with attempts to apply either one or other or both of these ideas, purporting to explain many and varied phenomena, while at the same time no adequate theories of the mechanism or cause of solution have been suggested. As a result therefore many of the so-called explanations are stated in terms which give no physical concept of the underlying idea, and as a consequence lack the definiteness which they should carry.

From the early investigations of Mendeléef² concerning the hydration of substances in aqueous solution there grew up numerous applications of this idea to solution properties in general. H. E. Armstrong³ attempted to explain the mechanism and velocities of inversion of sugars and esters on the view of mutual hydration of the participants in the reactions, to the complete exclusion of any ionic dissociation ideas⁴. Later H. C. Jones amplified these ideas to general solvation.⁵

Regarding these theories of hydration one point has been emphasised repeatedly, apparently as a necessary consequence of any view of hydration of a solute in solution. The exact form which this consequence takes, seems to have varied in different cases although it would appear that such was the result merely of terminology on a phenomenon about which we have no practical conception. Thus Jones (*loc. cit.*) concludes "that in solution a part of the solvent is combined with the dissolved substance and *no longer plays the role of solvent.*"⁶

Among the facts which led to this result two cases may be cited. Ordeman⁷ made determinations of the specific conductivity of solutions of potassium chloride and of calcium chloride, to which various amounts of other chlorides were added. It was found that the increase in conductivity was greater with potassium than with calcium chloride. Since however, the solutions had the same chloride ion concentration the shift of the dissociation due to the anions was the same in both cases and it was suggested that "the combined water in the solution of the hydrated salts is less associated than the free water, in which case the added salts would be less dissociated since the dissociating power changes with its own association, and further, this effect would be

¹ Contribution from the Havemeyer Chemical Laboratory, New York University.

² Z. physik. Chem., **1**, 273 (1887).

³ J. Chem. Soc., (1890) et seq.

⁴ Cf. Nature, **55**, 78 (1896).

⁵ Inter alia. "Hydrates in Aqueous Solution." Carnegie Inst. Pub. No. 60.

⁶ Author's italics.

⁷ Carnegie Inst. Pub. Nos. **230**, 161 (1915); **260**, 119 (1918).

greater the greater the concentration, since more combined water would then be present in the solution of calcium chloride."¹ The other example may be taken from the observations of Jones and Guy² who found that "combined water has less power to absorb in the region $1.05\text{--}1.2\mu$ than free or uncombined water," a fact confirmed later by Jones, Shaeffer and Paulus³ namely that "in some cases aqueous solutions of hydrated salts were forty percent more transparent than a comparable quantity of pure water."

Again, Lapworth⁴ as a result of reaction velocity measurements in hydrogen ion catalysis concludes "that water added to acids in less basic solvents reduces the concentration of the hydrogen ions, or on a less hypothetical basis, diminishes the availability of the acid for salt formation." This fact he correlates with a previous, more general, observation by Armstrong (*loc. cit.*) "that substances which act as dehydrants will have a concentrating effect on others which are hydrated in aqueous solutions." Jones and Lapworth⁵ also compare their results of the action of hydrochloric acid in ester hydrolysis in removing water from the system, with an earlier experiment by Berthelot and Péan de Saint-Gilles⁶ showing that the presence of barium chloride affects to a marked extent the proportion of benzoic ester hydrolysed by water, Berthelot adding "due perhaps to the affinity of barium chloride for water."

More recently Harned⁷ points out "that the activity coefficient of hydrochloric acid is greater in solutions of electrolytes which have higher hydration values or which when alone in aqueous solutions have higher activity coefficients," although he concludes later⁸ that neutral salt effect is probably due to the large decrease in the heat content of transfer and not to high hydration of the hydrogen ion, since it was found that neutral salt action is a function of the total ion activity and not that of the catalysing ion alone, a fact in opposition to the suggestion of Poma⁹ and Bjerrum¹⁰ who would account for it solely on a basis of hydration.

Finally Corran and Lewis¹¹ find that the activity of the chloride ion rises in presence of sucrose, which rise can be accounted for by a decrease in the total amount of water present, but that the amount of water of hydration need not be deducted, leading to the observation that the chloride ion "is soluble in the water of hydration of sucrose." This and other observations

¹ This explanation of the results would seem particularly interesting in view of the recent results of Harned: *J. Am. Chem. Soc.*, **47**, 930 (1925) who has shown indisputably, that the actual dissociation of water is increased very rapidly at first by salt addition; the effect of sodium chloride being somewhat greater than that of potassium chloride.

² Carnegie Inst. Pub. No. **190** (1913).

³ Carnegie Inst. Pub. No. **210** (1915).

⁴ *J. Chem. Soc.*, **93**, 2203 (1908).

⁵ *J. Chem. Soc.*, **99**, 1429 (1911).

⁶ *Ann. Chim. Phys.*, **68**, 225 (1863).

⁷ Taylor: "Treatise on Physical Chemistry," p. 767 (1924).

⁸ *J. Am. Chem. Soc.*, **42**, 1808 (1920).

⁹ *Z. physik. Chem.*, **87**, 197 (1914).

¹⁰ *Z. anorg. Chem.*, **109**, 295 (1920); cf. also Thomas and Baldwin: *J. Am. Chem. Soc.*, **41**, 1981 (1919).

¹¹ *J. Am. Chem. Soc.*, **44**, 1673 (1922).

in Lewis' laboratory have led to the interesting conclusions summarised by Garrett and Lewis¹, "that (1) the water of hydration of sucrose is *not* free to act as solvent for the hydroxy (valeric) acid molecule; (2) the water of hydration of potassium and lithium chlorides *is* available as solvent for the hydroxy acid molecule; (3) hydrogen ion is *insoluble* in the water of hydration of sucrose and also *insoluble* in the water of hydration of potassium and lithium chlorides; (4) potassium and chloride ions, both of which are hydrated, are soluble in the water of hydration of sucrose; (5) sucrose tetrahydrate is soluble in the water of hydration of acetic acid." More generally they suggest that the solvent power of water of hydration cannot be related simply to the electric charge in the case of molecules but is apparently specific of both colliding individuals, so that when both colliding individuals are hydrated, mutual solubility occurs.

From such a varied collection of observations, but one result can be drawn. However unjustifiable some of the conclusions may be in the light of more recent work, one point would seem certain, namely, that if hydration does occur, there is some difference between the combined water and that in the free state. Whether this difference may be expressed either as dissociating power, light absorbing power, activity or solvent power would not appear certain. Some of the facts are based on various theories and mechanisms of reaction which if incorrect would vitiate the conclusions. Thus in ion catalysis Rice² would account for all mechanisms solely on the basis of unhydrated ions, a theory which will account for the observed facts and which does not necessitate a consideration of the possibility even, of solvent power of the water of hydration.

Regarding these results solely in the light of their practical significance and attempting to visualise the various points suggested, one is forced to fall back on some theory of solution, a problem about which our knowledge is most meagre. The major portion of the advance in the theories of solution has been made on the assumption that bodies in solution behave in many respects like the same body in the gaseous state. Now the dynamical condition of a molecule in solution is utterly different from that in the gaseous state, in that, in solution a molecule is never outside the range of attraction of its neighbours but is continually passing from one neighbour to another by collision. If we consider that the molecules in a solution move with velocities comparable with those in the gaseous state, which is probable, since the solvent molecules at least, escape into the surrounding vapour, then it would seem that from the rate of diffusion of a substance in solution the molecules do not progress as though they were capable of passing freely through the solvent molecules, however possible such a passage might be on the Bohr theory. We are led therefore to consider a solution as composed of solvent molecules, between the interstices of which, the solute is continually moving. Nevertheless it appears that the solute molecules, at least in so far as they produce osmotic pressure, may be regarded as occupying the whole volume

¹ J. Am. Chem. Soc., **45**, 1101 (1923).

² J. Am. Chem. Soc., **45**, 2808 (1923); **46**, 2405 (1924).

of the solution, since this pressure may be calculated from the gaseous pressure which they produce when alone in such a volume.

Such a simple view however, leads to difficulties when we come to consider a saturated solution. Obviously a saturated solution is not one in which all the interspaces between the solvent molecules are occupied by solute, since a saturated solution of one substance can still dissolve a certain amount of a second substance, irrespective of the absolute size of the molecules of the two substances, and independent therefore, of any question of packing of the solute molecules in the solvent interspaces. Furthermore in osmotic phenomena it seems reasonable to ascribe attractive forces, whether they be "capillary" forces or electrostatic, to the solvent and solute molecules to account for the movement of the solvent molecules through the membrane. The solvation theory of osmosis would, on this basis, be a special case, in which permanent chemical combination occurred between the solvent and solute. Now from our knowledge of the hydration values of various substances in aqueous solutions¹ and their solubilities, it is not conceivable that any hydration theory can account for the cause of solution and solubility and there remains only the view of attractive forces between the molecules, definite in magnitude for every pair of solvent and solute molecules. When these attractive forces are satisfied the solvent is said to be saturated with the solute, yet at the same time there still remain these forces between the solvent for a second solute, the neutralising of which will be modified somewhat by the secondary influence of the solute molecules of both kinds on one another. The condition would therefore seem parallel again to that in gaseous mixtures in so far as attractive forces between the molecules exist. On the simplest theory then, it is evident that the effect of addition of a solute to a solvent must take into consideration the relative attractions, magnitudes and possibly to some extent the change in available spacing of the molecules.

Such a view of solution processes is in agreement with the more recent ideas of Born and Landé² and of Fajans³. It was shown that quantitative relationships hold between gaseous ions and ions in solution, when the change in electrical field outside the ion, due merely to change in the dielectric capacity of the medium, is taken into account. The actual process of solution of a gaseous ion is regarded⁴ as the condensation of an unknown number of water molecules around the ion comparable with electrostriction. It is supposed that by means of the charge on the ion, the oppositely charged parts of the polar water molecules in the immediate neighbourhood are oriented towards the ion, the similarly charged parts of the water molecules being repelled from the ion, these in turn repelling other molecules in their vicinity. A solution of an electrolyte in water would therefore be an electrically polarised system, the solubility depending on the extent to which this polarisation

¹ Cf. Washburn: *J. Am. Chem. Soc.*, **31**, 322 (1909).

² *Ber. deutsch physik. Ges.*, **1918** et seq; *Z. Physik*, **1920** et seq.

³ *Ber. deutsch. physik. Ges.*, **21**, 542 (1919); Compare also Debye and Hückel: *Physik. Z.*, **24**, 185; and Debye: **24**, 334 (1923).

⁴ Fajans: loc. cit.

may proceed. Further this would depend on the size of the ions (as shown by Born¹ which governs the distances through which the electrical forces are operating.

There remains one other theory which offers a suggestion as to the fundamental cause of solution, namely, that due to Kruger², which indicates that radiation, usually of the infra-red region, plays a rôle in these processes. Kruger deduced a relationship between the dilution of the solution and the dielectric constant of the solvent, which, qualitatively at least, agrees with known observations; for example, water with a high dielectric constant is our best known solvent. The application of these ideas to the kinetics of solution has not however received as yet the attention of the proponents of the radiation theory of chemical reaction³, although following the same line of reasoning as they employ, namely a quantisation of the energy change involved, and using data on the rate of solution obtained in Nernst's laboratory⁴ the calculated wave lengths fall in the infra-red region. Temperature coefficients of the order of 1.5 to 1.8 per 10°C rise were obtained for such substances as benzoic acid and lead chloride dissolving in water. The wave lengths calculated from these temperature coefficients are 3.9 μ and 2.7 μ respectively, both of which are in the infra-red region where the radiation density is greatest at room temperatures. That the rate of solution could be affected however, by exposure to infra-red radiation seems well nigh impossible, especially if the Nernst-Noyes-Whitney view of the rate of solution being the rate of diffusion of the saturated solution away from the solute, is true. One point nevertheless, suggests itself, namely, that of an interpretation of the above calculated critical increments or energies of activation (which are of the order of 7,000 to 10,000 calories) being a measure of the statistical attractive forces between the solvent and solute molecules, for it is evident that the rate of diffusion must depend to a large extent on these forces.

With these theories of solution in mind, attempts to picture some of the statements made previously with regard to water of hydration, such for example as its ability to act as solvent, do not lead very far. It is difficult in fact, on any theory, to see how the few molecules of water attached to an ion or a molecule can act as a solvent for another molecule. On the electrical view apparently, an ion or a molecule becomes 'hydrated' (in the Born sense), that is, goes into solution, when an electrical polarisation is effected. No suggestions are available of the number of water molecules necessary to complete this 'hydration,' although comparison of the data on the heat of hydration of a gaseous ion with those on the heat quantities usually attributed to the formation of ion hydrates of definite stoichiometric composition would seem to point to a much larger number of molecules being involved in the former case. It would be improbable therefore, that the few molecules of

¹ Ber. deutsch. physik. Ges., **21**, 679 (1919). Compare also forth-coming publication by Hückel on change in dielectric constant with concentration.

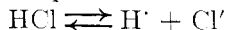
² Z. Elektrochem., **17**, 453 (1911).

³ Cf. Lewis' "System of Physical Chemistry," 3rd. Ed. Vol. II. p. 232.

⁴ Brunner and St. Tolloczko: Z. physik. Chem., **35**, 283 (1900).

water of hydration of an ion or a molecule in aqueous solution, which molecules are already bound and probably therefore oriented in a definite manner, could ever satisfy the requirements of a solvent for another ion or molecule. The confirmation which the electrical treatment of Born and Fajans has received up to the present seems to have proved its reliability and utility.

An attempt therefore, was made to confirm the facts by a totally different method¹. Consider the system benzene: water with hydrogen chloride distributed between the two phases. In the aqueous layer there is an equilibrium which may be expressed by the equation:



According to Moran and Lewis (*loc. cit.*) hydrogen ion is insoluble in the water of hydration of various electrolytes. On adding these electrolytes

therefore to the aqueous layer one should remove water capable of dissolving hydrogen ion. The concentration of the hydrogen ion would thereby be increased in the remaining water. This would cause an increase in the concentration of undissociated hydrochloric acid, or on the complete dissociation theory, would increase the probability that a hydrogen and a chloride ion were under mutual electrostatic influences. The disturbance of the equilibrium obtaining in the aqueous layer would be reflected in the benzene layer, the effect being measurable by a change in the distribution ratio of the hydrogen chloride between the two solvents.

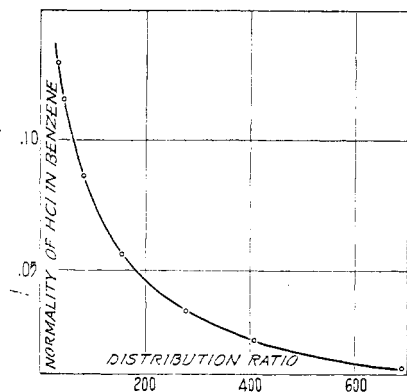


FIG. 1

Hydrogen Chloride in Benzene and Aqueous Solutions

A number of solutions were made up of concentrated hydrochloric acid containing several electrolytes and glycerol, all being more or less hydrated in solution. These solutions were allowed to attain equilibrium with benzene by repeatedly shaking over a period of several days, and their distribution constants found by titration of the two layers in each case with standard sodium hydroxide.

Beckmann² finds that the greater the normality of hydrogen chloride in the benzene layer under such circumstances, the more nearly does the hydrogen chloride tend to form single molecules. The distribution ratio calculated directly from the titre of each layer does not, therefore, yield a constant. For our purpose however, it does not seem necessary to obtain one. The difficulty is most easily overcome by finding the value of the 'constant' for different

¹ Much work along the same line has been carried out by Szyzskowski using in all cases however, weak acids only. Cf. Meddel. från. K. Vet. Akad.:s. Nobelinstitut. 3, Nos. 2, 3, 4, 5, 9, 10, 11 (1915-1918).

² Z. physik. Chem., 60, 385 (1907).

concentrations of hydrogen chloride in the benzene layer. To this end a series of solutions of aqueous hydrochloric acid of different strengths were taken and their partition coefficients obtained with benzene.

The ratio calculated from the observed titrations of the two layers is shown in Fig. 1 plotted against normality of hydrogen chloride in the benzene layer.

From the slope of the curve, it can be seen that the value of the ratio changes rapidly with a small change in the hydrogen chloride concentration of the benzene.

The results obtained in the distribution experiments using aqueous solutions of hydrogen chloride together with the hydrated bodies are given in Table I, the concentrations of added substance being approximately normal in each case.

TABLE I
Normality of HCl

Added Compound (Approx. 1N)	Phase	Normality of HCl	Ratio	Ratio for pure HCl
NaCl	Benzene	0.072	161.4	158
	Water	11.63		
KCl	Benzene	0.0716	160.4	160
	Water	11.49		
LiCl	Benzene	0.130	83.9	85
	Water	10.92		
RbCl	Benzene	0.0714	157.2	160
	Water	11.22		
CaCl ₂	Benzene	0.1161	98.2	95
	Water	11.40		
BaCl ₂	Benzene	0.0698	166.5	165
	Water	11.61		
Glycerol	Benzene	0.0740	153.8	153
	Water	11.37		

The third column gives the normality of hydrogen chloride in the two layers taken directly from the titrations with standard sodium hydroxide. Column 4 is the direct ratio of these, namely, water: benzene. In column 5 is added the ratio observed in the previous case using pure aqueous hydrochloric acid and benzene; the ratio given being taken from the graph when the concentration of hydrogen chloride in the benzene layer in the two cases is the same. In this way a true comparison of the aqueous solutions can be made, that is, of pure hydrochloric acid on the one hand and a hydrochloric acid solution containing a hydrated substance on the other. That the actual value of the ratio is different in the different salt solutions is to be expected when it is observed that the total hydrogen chloride concentration varies slightly from case to case, a variation magnified greatly in the value of the ratio owing to the smallness of the benzene concentration.

The remarkable result however, is the agreement between the last two columns shown. Since the observed ratio in the case of the different solutions, agrees with that for pure hydrochloric acid when the concentration in

the benzene layer is the same in each case, it follows that the concentration in the aqueous layer must also be the same in the two cases. In other words the neutral salt or glycerol solution of hydrogen chloride is behaving in exactly the same manner as a pure aqueous solution of hydrogen chloride, and the presence of the added compound whether largely or slightly hydrated is without effect on the distribution.

At first sight such a result would appear to deny many of the facts stated earlier in the paper. The possibility of interpreting the statement specifically, however, in any one regard is not obvious. It might appear for example that the activity of hydrochloric acid in neutral salt solution was the same as that in pure aqueous solution (a fact denied by Harned), if we regard the distribution law from the point of view of the activity concept namely, that the ratio of the activity of the distributed species in the two phases is constant. It can nevertheless be argued that the concentration of the hydrogen chloride in the aqueous layer is so great that even the activity concept fails to hold rigidly in this case, as in others dealing with strong electrolytes, which by its failure would vitiate the observation made. Or again, to take another example relative to the ability of water of hydration to act as a solvent, although such an effect is noticeable with more dilute acid solutions it would in all probability be negligibly small with such concentrated ones.

The apparent fact that the neutral salt solution was behaving in the same manner as a pure aqueous hydrogen chloride solution having the same concentration of HCl suggested at once that confirmation might be obtained from a determination of the vapour pressure of the hydrogen chloride over the two solutions. Absolute data on the vapour pressures of hydrogen chloride over its aqueous solution, especially at such concentrations as were used in this work, are scanty and unconvincing. The reason becomes obvious on analysing the data at lower concentrations. Dobson and Masson¹ give the partial pressure of hydrogen chloride over 10.52 N HCl as between 35 and 40 mms., but state that no stress may be laid on these values. Bates and Kirschman² give a value of 4.20 mms. for 10 N HCl, both these values being given at 25°C. Now according to the solubility data of Roscoe and Ditmar the maximum strength of an HCl solution at 25°C is about 19 N, so that the increase in partial pressure of hydrogen chloride over solutions from 10 to 19 N must be extremely rapid and hence the accuracy of individual determinations uncertain. It was considered doubtful therefore, whether the effect of neutral salt would be noticeable on the partial pressure of 12 N HCl, the strength used in the previous work, since the concentration of salt is small even in the saturated solution, and the partial pressure of the hydrogen chloride increasing rapidly.

A few comparative tests however, were made by bubbling a fixed volume of dry air through the hydrogen chloride solutions and absorbing the acid carried over in standard sodium hydroxide. Care was taken to avoid any

¹ J. Chem. Soc., **125**, 668 (1924).

² J. Am. Chem. Soc., **41**, 1991 (1919).

spray being carried over by passing the air from the hydrogen chloride bottle through a small column containing glass wool which was previously saturated with hydrogen chloride vapour, the whole apparatus being completely immersed in a thermostat at 25°C. Table II gives the results obtained in cubic centimetres of the standard alkali used.

TABLE II	
Solution	Vapour Pressure in ccs. Alkali.
12 N HCl	61.85
	61.27
12 N HCl + N NaCl	61.50
	60.87
12 N HCl + N KCl	61.58
	(59.40)

The results although only comparative would appear to show that the vapour pressure of the hydrogen chloride was not appreciably affected by the presence of this quantity of added salt in such concentrated solutions of acid. What the effect would be on more dilute solutions cannot be foretold but the two effects herein observed for concentrated solutions are mutually confirmatory.

It seems definite therefore that the many facts quoted earlier in the paper are not proven generally and that doubt must be cast on the various explanations offered. Recent work by Linderström-Lang¹ on the influence of neutral substances on the solubility of succinic and boric acids leads to the view that hydration as playing the leading part in the salting out process must be rejected. The causes of variation in the solubility may be explained on the basis of Debye's views on the nature of the cohesive forces between the ions the specificity of an ion being due not to hydration but to these forces which will depend on their structure, size and polarisability.

Further work along these lines is at present in progress using smaller concentrations of acid and with other acids also towards a more definite elucidation of the problem.

Summary

(1) Numerous cases have been quoted where evidence is suggested that the water combined as water of hydration, differs from ordinary water in many of its properties.

(2) The interpretation of these examples from the point of view of modern theories of solution is discussed and criticisms offered.

(3) From a study of the effect of various hydrated bodies on the distribution of hydrogen chloride between benzene and water it is suggested that aqueous solutions of such bodies behave precisely as does pure water, indicating no dissimilarity between the so-called combined and free water.

(4) This fact appears also to be confirmed by a study of the effect of neutral salts on the partial pressure of hydrogen chloride over concentrated hydrochloric acid solutions. Further work is in progress.

New York, N. Y.

¹ Compt. rend. Trav. Lab. Carlsberg, **15**, 1 (1924).