

THE MOLECULAR STRUCTURE OF WATER

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Because of the importance of water in the theoretical speculations as well as the practical routine of chemists, a review of the theories concerning its structure is pertinent. The physical properties of liquid water are different from those of most liquids. As the distinction between normal and associated liquids has developed, water has been accepted as an excellent example of the second class. A record of the development of the various theories of the liquid state, as they have been proposed to explain particular physical properties, would elucidate the case of water. All these criteria of association qualitatively classify water as associated yet the different quantitative methods do not yield concordant results as to the extent of that association (1). Hence, we shall primarily consider those theories which deal with water itself, reviewing the hypotheses that have been advanced concerning the equilibria existing in the liquid state.

“ICE MOLECULES”

Whiting (2) was the first to speak of the possibility of “solid particles” in liquid water. In a thesis on a “Theory of Cohesion” published in 1884, he developed mathematically a theory of cohesion based on the action of three pressures, an external pressure, a pressure caused by the kinetic motion of the particles, and a pressure due to the affinities of one molecule for another. He assumed that cohesive forces between two particles depend upon the fourth power of the distance between them. From these assumptions he derived formulas connecting the physical properties of a liquid, such as volume change with temperature and pressure, latent heat, specific heat, critical phenomena, etc. Because the data for water did not satisfy his equations which

were applicable to most liquids, he came to the conclusion that only those liquids which suffered no molecular rearrangements when heated or put under pressure satisfied his equations. He applied the theory of probability to liquids near their freezing point, and found that in a liquid state there are some particles corresponding to the solid state and in a solid state some particles corresponding to a liquid state. What distinguishes a solid from a liquid is not, according to this theory, the fact that all particles are either solid or liquid, but simply that the rate of solidification or of liquefaction is in excess of the other process. The existence of an indefinite number of these small solid particles would have a marked influence on volume changes provided they were different in volume from those of the liquid state. But water expands on solidification, so that if the number of solid particles increases with decrease in temperature, the liquid would expand on cooling.

Whiting continues,

It may be allowable to suggest, that from almost any point of view, there will be in melting ice, only from 50 to 70 per cent of solid particles, and in freezing water nearly one-half as many, but in boiling water not more than one-third; so the number which disappear in melting is not more than twice the number which are eliminated when the liquid is raised to boiling. The expansion, therefore, from 0° to 100° instead of being 1.04, is probably from 0.08 to 1.10 and the real coefficient of expansion at 0° is from 0.0006 to 0.0008, increasing regularly with the temperature, as in the case of any ordinary liquid.

In those early days Julius Thomsen (3) concluded that water molecules are twice as heavy as vapor molecules, as did Raoult (4) from a study of freezing points of solutions. Armstrong (5) in 1888 advanced the idea that liquids in general are probably made up of complexes of the fundamental gas molecules through the action of residual affinity.

Vernon (6), quite independently, explained the temperature of maximum density by the presence of "water molecules aggregating together," and possessing a density smaller than water but larger than ice molecules. The water molecules were supposed to be $(\text{H}_2\text{O})_2$ while the complexes were given a formula

(H₂O)₄. He also demonstrated from specific heat data that the increase in complexity of the molecules is accompanied by an evolution of heat.

To Röntgen (7) is commonly ascribed the first suggestion of "ice molecules" in liquid water. His paper followed that of Whiting by eight years but was very much more extensive in explaining the properties of this interesting liquid. He postulated that water is a saturated solution of ice molecules and that the concentration depends on the temperature, a decrease in temperature favoring the formation of the more complex ice molecules. He assumed further that the change in molecular state from complex to simple molecules, corresponding to melting of ice, has the result of decreasing the volume. On these assumptions he explained the point of maximum density. If water below 4° is heated, the volume would be changed by two actions; first there would be contraction due to the breaking up of the bulky complex molecules, and secondly there would be an expansion due to thermal expansion of the liquid molecules. If the former is in excess of the latter, the liquid would contract on heating; but if the latter is in excess of the former, there would be an expansion on heating. This is what is assumed to occur below and above the point of maximum density.

Röntgen said, from the analogy of ordinary saturated solutions, that pressure would decrease the number of ice molecules, and so cause a contraction. For a given pressure, this would be greater the lower the temperature. The compressibility of a normal liquid is smaller the lower the temperature. So it follows that for water there is a point of minimum compressibility at some temperature above the freezing point. Such a point is found at about 50°.

A third anomaly was the fact that the thermal coefficient of expansion of water at pressures of 3000 atmospheres is opposite in sign to that of other liquids, for it increases with increasing pressure. Normally this would decrease with increasing pressure, as does the compressibility. If the pressure breaks up the complex molecules fast enough for the resulting increase of volume to exceed the decrease due to the normal action of pressure, then

the thermal coefficient would increase with increasing pressure, as it does in the case of water.

Röntgen claimed that on the assumption that the number of ice molecules is decreased by pressure, the maximum density of water would occur at a lower temperature under pressure (as found by Amagat and others) and the freezing point would be lowered by pressure. Furthermore, within a certain interval of temperature, water subjected to an increase in pressure, would cause a cooling, on the assumption that the change of ice molecules to simple molecules uses up heat.

The last anomaly explained by Röntgen was the decreasing viscosity of water with increasing pressure. This was accomplished by the assumption that the simple molecules had a smaller viscosity than the ice molecules.

These postulates have been the foundation of practically all of the theories concerning the molecular state of water.

THE CONCEPT OF EQUILIBRIUM

The principles of thermodynamics were applied to the problem by Van Laar (8) who, after having accepted Ramsay and Shields' values for the quantitative degree of association, concluded that an equilibrium exists between double and single molecules, their proportions changing with conditions as postulated by Röntgen. Furthermore, when a second material like alcohol is added, he supposed that some of the double molecules are broken into single molecules, with a resultant contraction.

Röntgen's postulates were used by de Coppet (9) and Witt (10) to explain the displacement of the temperature of maximum density in solution. Witt also attempted to explain heats of solution, abnormal lowerings of the vapor pressure and excessive increases of osmotic pressure as they changed with concentration. He believed that this simple water molecule is $(\text{H}_2\text{O})_2$ while the ice molecule is $(\text{H}_2\text{O})_3$.

Sutherland (11), in 1901, presented a very interesting attempt to determine the relative amounts of the complex molecules under various conditions. His calculations led him to believe that water is a binary mixture of trihydrol $(\text{H}_2\text{O})_3$ and dihydrol

$(\text{H}_2\text{O})_2$ existing in a dynamic equilibrium. Due to the hexagonal structure of ice, the solid molecules (those having the greater volume) were supposed to be trihydrol, $(\text{H}_2\text{O})_3$. From the density of ice and the usual expansion resulting upon melting the solid of a normal liquid, he calculated the probable density of the trihydrol molecules in the liquid state. The change in density of the simpler molecules with a change of temperature was assumed to be given by the tangent drawn to the density-temperature curve at 100° . Then by the use of Mendeléeff's equation for the expansion of normal liquids and the mixture law he calculated the various amounts of the different molecular species existing at any temperature. At 0° the percent of $(\text{H}_2\text{O})_3$ was 37.5, at 20° 32.1 per cent, and at 100° 21.7 per cent. At the critical temperature the liquid was supposed to be nearly pure dihydrol. From this table of composition the various physical properties of the two components were calculated. The change in composition with a change in pressure was also calculated, and resulted in the prediction of the pressure above which water would behave like a normal liquid composed of only one sort of molecule, dihydrol.

Sutherland reasoned further that if pressure causes dissociation of complex molecules, then surface tension would produce a layer of more highly associated molecules. At temperatures below 40° this layer was supposed to be pure trihydrol.

The abnormally large heat changes accompanying a change in state are further evidence that the molecular nature of water is complex. The heat of fusion must include the heat of reaction of di- to trihydrol, while the heat of vaporization must include the corresponding change from dihydrol to monohydrol (water vapor molecules). Sutherland estimated each of these heats of reaction.

The decrease in viscosity of water with an increase of pressure or temperature was explained by the assumption that the smaller particles formed by the breaking up of the complexes have a smaller viscosity than the aggregates. The fact that the viscosity of some dilute solutions is smaller than that of pure water was explained by the breaking up of some of the trihydrol under the action of the solute.

The fact that the freezing point occurs at a definite temperature even though the liquid consisted of di- and trihydrol in dynamic equilibrium gave Sutherland some difficulty. He suggested that this is caused by some sort of molecular resonance.

The changes in volume due to changes in polymerization have been considered by Richards (12) in connection with his lucid explanation of cohesive forces as they affect volume. Here the union of molecules was supposed to take place through the forces between oxygen atoms.

Hudson (13) explained the constant temperature of freezing by assuming that the ice molecules have a definite solubility in the water as well as a definite equilibrium concentration, both of these concentrations varying with the temperature. When they are equal (at 0° in pure water) solid appears. Above 0° the equilibrium concentration would be less than the solubility. If a second chemical substance is introduced, this is supposed to decrease the amount of ice molecules, making it necessary to cool the solution to a lower temperature before the equilibrium concentration reaches the saturation point of the ice molecules.

In 1908 Armstrong (14) attacked the problem from the chemical point of view and suggested the possibility of the existence of isomeric water molecules of the same molecular complexity but with different structure. These molecules have different activities depending upon their chemical structure in a manner similar to organic compounds. For example, the active isomers might

be hydrol (OH_2) or hydronol $\left(\begin{array}{c} \text{H} \\ \diagup \text{O} \\ \text{H}_2\text{O} \\ \diagdown \text{O} \\ \text{OH} \end{array} \right)$ while the inactive

molecules would be represented by closed systems with oxygen atoms joined to oxygens, each having a valence of four. These were called hydrones. He believed that in solutions of electrolytes the solute changed the proportions of these constituents and that the ions combined with the active forms of water. From this point of view he studied the volume changes on neutralizing acids and bases, the effects of salts on optical activity of sugar solutions, etc. More recent views will be discussed later.

THE FARADAY SYMPOSIUM

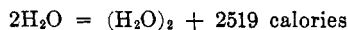
In 1910 the Faraday Society (15) held a symposium on the structure of water. Papers were presented by Walden, Guye, Bousfield and Lowry, Sutherland, and Nernst. Walden showed that water is not an electrolyte except in solutions where its amphoteric nature allows it to form some kind of a "salt" with the other constituent. Guye presented his quantitative method of determining association in the liquid state, based on the assumptions that association existing in the vapor state proves association in the liquid, and that liquid water is made up of two sorts of molecules, a single and a double one. At 100° the association factor was equal to 1.86. Sutherland reiterated his belief that liquid water is a binary mixture of molecules, suggesting that any $(\text{H}_2\text{O})_1$ was completely ionized into H^+ and OH^- .

Bousfield and Lowry presented an important paper in which they suggested that water is a ternary mixture, composed at low temperatures of $(\text{H}_2\text{O})_3$ and $(\text{H}_2\text{O})_2$, but at higher temperatures of $(\text{H}_2\text{O})_2$ and $(\text{H}_2\text{O})_1$. This conclusion was arrived at by considering water as the limiting case of a series of solutions of sodium hydroxide, where water is the most complex system, the complexity decreasing with increased concentration, until at 12 per cent the curves which represent changes in solution volume with temperature could be represented by a parabolic formula and at 42.5 per cent by a linear function over the temperature range 0° to 100°. The straight line, which is the limit of these curves, is tangent to the specific volume temperature curve for water at about 30°. (The solution volume of a solute is defined as the increase in the volume of the liquid which takes place when 1 gram of the solute is dissolved in 100 cc. of the solvent.) At 60° the specific volume curve for water begins to become abnormal, which was explained by the presence of increasing amounts of steam molecules. So Bousfield and Lowry differed from Sutherland in thinking that the line showing the normal behavior of pure water molecules is tangent to the actual curve at 30° rather than at 100°.

The solutions studied were those of sugar, acetic acid, and such

strong electrolytes as sodium hydroxide, silver nitrate, lithium chloride, etc. In such solutions the possibility of hydrate formation must be considered. In the curves obtained for the salts, there are decided maxima, which flatten out as the concentration of solute decreases. In such cases the curve for water is the simplest of the family. Hydration of the solute was used to explain these curves.

The last paper presented at the symposium was by Nernst, on the specific heat of steam, water, and ice. He showed that the data could be explained by accepting the expression:



At the end of the discussion, Professor James Walker, the chairman of the meeting said:

I should think as a result of this discussion, one will soon find even in the textbooks that while ice is trihydrol, and steam monohydrol, liquid water is mostly dihydrol with some trihydrol in it near the freezing point and a little monohydrol near the boiling point.

Bousfield has used his theory of the structure of liquid water in several later papers. In the first of these (16) he pointed out that there is probably an intimate connection between the vapor pressure of water and the proportion of steam molecules in the liquid; that there was little doubt that the proportion of steam as well as ice molecules is reduced by the solution in water of any solute, and that this is connected with the reduction of the vapor pressure. He again pointed out (17) the "remarkable fact that steam molecules, like ice molecules, must be considered as bulky molecules." In the second paper (18) osmotic pressure was attributed to the thermal agitation of the vapor molecules $(\text{H}_2\text{O})_1$. The addition of a solute was said to be accompanied by a shift in the equilibrium conditions of the liquid water, which results in the depression of the vapor pressure and of the freezing point.

CRYOSCOPIC DETERMINATIONS

Various other methods of attack have been used in attempting to determine the molecular state of water. One that would come

to mind immediately would be that of cryoscopic determinations (19). On the basis of the theories outlined, the assumption that the molecular state in pure liquid would be the same as that existing in the presence of a large excess of a second substance is false. The apparent molecular weight of the water, of course, varies with the concentration of the solution. With solvents such as p-toluidine, phenol, bromoform, methyl oxalate, ethylene bromide, and veratrol the calculated molecular weight of the water varies from 17.6 to 35.9. Bruni and Amadori (19) concluded that in nondissociating solvents water forms complex molecules and if double molecules exist exclusively, they do so only in very concentrated solutions, while in all solvents water tends to form simple molecules of monohydrate in dilute solutions. Oddo and Scandola (20) in 1910 critically reviewed the cryoscopic determinations and decided that in practically all solvents the water exists as $(\text{H}_2\text{O})_2$ unless it combined with the solvent.

From a study of the system: water, ether, and succinic acid, Forbes and Coolidge (21) estimated that the association factor of the water dissolved in the ether is a little less than two.

THE CRYSTALLINE HYDRATES

Still another method of attack has been the study of crystalline hydrates, there being a supposed relation between water of crystallization and liquid water. One of the most common of the early attempts was to calculate the density of the water held in the crystal and then classify it as a particular form of hydrate. Pickering (22) said that the density is the same as that of ice, believing that ice is not an aggregate of the water molecule but an entirely different compound. A study of specific heats of hydrates confirmed his views. Thorpe and Watts (23) said that water of crystallization has a density of 1.24. Sutherland (24) calculated that the density of water held in $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ is 1.31 and thus about the average of 31 other hydrates, as determined by Clarke (25). As a consequence, he assumed this to be the density of solid monohydrate. Biltz (26) has recently calculated the molecular volume of the water in $\text{CuSO}_4 \cdot 2\text{H}_2\text{O}$ to be 13.7 cc. Rosenstiehl (27) made an extensive study of some 179 hydrated

salts and concluded from the numbers of water molecules lost in each step of hydration that liquid water is a ternary mixture of $(\text{H}_2\text{O})_1$, $(\text{H}_2\text{O})_2$, and $(\text{H}_2\text{O})_3$.

The x-ray analysis of hydrates shows the futility of these attempts. What data there are would show (28) that the water is present as H_2O units. In the hexahydrate of zinc bromate, for instance, the six H_2O groups are all equivalent and have a similar arrangement, probably about the zinc atom. In the alums the twelve water molecules fall into two groups of six equivalent molecules, probably arranged about the metal atoms.

THE STRUCTURE OF ICE

We have seen in the preceding discussion that the molecular unit of ice has been assumed to be trihydrol. This is affirmed by Fielding (29) while Duclaux (30) has suggested that its composition is between $(\text{H}_2\text{O})_6$ and $(\text{H}_2\text{O})_{23}$.

The researches of Tammann (31) and Bridgman (32) on water under high pressure and the evidence for believing the existence of several forms of ice are well known. They have studied water under high pressures over a large range of temperature and have found that there are five different kinds of ice, each one stable under particular conditions of pressure and temperature. Tammann believes that it exists in several forms which fall into two groups: (a) those which are lighter than liquid water, and (b) those which are heavier than liquid water. He concludes that ice belonging to group (a) separates only from liquid water rich in polymolecules, while those belonging to class (b) form from water containing an abundance of simple molecules. Ordinary ice, called I, belongs to group (a). Ice II and III he concludes to have the same form and to fall in class (b). He believes that liquid water under pressure behaves like a two component liquid.

In the papers on water, mentioned above, Bridgman discussed many of the abnormalities of water which change in magnitude with pressure and temperature. It was shown that water passes from an abnormal to a normal liquid as the pressure and the temperature increase; for instance, the minimum of compressibility at 50° is eliminated as the pressure increases. The point

of maximum density, which is at 4° at atmospheric pressure, is depressed rapidly by increasing pressure until it has fallen below the freezing point at 300 kgm. per square centimeter. These abnormalities of changes in volume with pressure and temperature were explained on the basis of polymerization, the presence of only two kinds of particles being assumed.

At temperatures near the melting point Tammann (33) believes that diffusion in a crystal occurs so that the molecular weight of a crystal near its melting point may be discussed. He calculated from Walden's (34) rule, admitting the doubtfulness of its application, that the molecular formulas of the ice I, III, IV, and VI are $(\text{H}_2\text{O})_3$, adding that the differences in the ices are due to isomerism rather than polymerism. He further concluded that only such molecules form crystals as exist in the liquid.

With the application of x-rays to the study of crystals of polar substances our concept of molecular weight in the solid state has little significance, giving place to the well known lattice structure in which molecules are indiscernible. The x-ray analyses of ice have yielded divergent results. A Laue photograph by Rinne (35) assigned ice to the hexagonal system with an axial ratio of $a : c = 1 : 1.678$. From an assumption that the crystals are not twinned, Gross (36) found that a unit cell containing two molecules of H_2O with axial ratio of 1.60 is compatible with the Laue photograph. According to the spectrometric results of St. John (37), the unit cell contains four molecules of H_2O with a ratio $a : c = 1 : 1.4026$. The powder photographs of Dennison (38) have been interpreted to yield a unit of yet another size, having an axial ratio of 1.62. The close approximation of this axial ratio to the ratio for the closely packed grouping of spheres (1:1.633) was taken as an indication that the molecules of water are associated into $(\text{H}_2\text{O})_2$ groups (39) which are themselves closely packed.

These data of Dennison have been used to confirm the structure of Bragg (40), arrived at by independent calculation. Bragg believes that no molecular unit exists in ice, that each oxygen atom is at the center of gravity of four neighboring oxygen atoms, from each of which it is separated by a hydrogen atom. In

organic liquids (41) two, three, or four molecules may exist as such in a crystal.

Wyckoff (42) in reviewing these determinations concluded that there is such serious conflict among the reported experimental data that "consequently nothing definite can be considered as known about its atomic arrangement."

VAPOR DENSITY EVIDENCE

Until recently it has been believed (43) that water in the vapor state is composed principally of single molecules but that there is a certain quantity of double molecules also. In fact, Guye's (44) method of determining the extent of association of a liquid was dependent upon the concentration of associated molecules in the vapor. Bose (45) calculated from the density determinations of Kornatz the concentration of double molecules to be about 10 per cent from 0° to 200°, while Oddo (46) assumed dissociation below 32° C. and association above that temperature in order to explain the data (41.4 per cent of $(\text{H}_2\text{O})_2$ at 270°).

Recently, however, both Kendall (47) and Menzies (48) have concluded from a recalculation of the old vapor density values that there is no evidence for the existence of double molecules when the densities are corrected for deviations from the perfect gas law. Shirai (49) confirmed this conclusion for the temperature range 80° to 140°. However, new determinations of density with an accuracy within 0.1 per cent at atmospheric pressure and at a temperature range from 98° to 200° have been reported by Maass and Mennie (50). The results show greater divergence from the ideal density than can be accounted for on the basis of the equation of state. As a consequence they have adopted the hypothesis of polymerization with the formation of double molecules. This association in the vicinity of 100° and 1 atmosphere pressure was estimated to be less than 0.9 per cent.

Gillet (51) has attempted to extend the fundamental portions of the theory of the polymerization of water to both real and colloidal solutions, but made many unreasonable assumptions.

RECENT THEORIES

H. E. Armstrong has long been a proponent of the marvelous nature of water and has pointed out on every possible occasion the neglect which chemists have shown in considering it a mere inert solvent. The development of his views concerning water and his attack on the theory of ionization since 1888 are to be found in his very recent collection of essays, "The Art and Principles of Chemistry" (52). He believes that water is a complex mixture saturated with the "gas" hydrone, OH_2 , which may become active under the influence of a dissolved substance. The relative proportion of this molecular species, either in water or an aqueous solution, is supposed to be measured by the vapor pressure. In a solution the hydrone molecules will be "distributed"

upon the solute, forming $\text{M} \begin{array}{l} \text{H} \\ \text{OH} \end{array}$ if the solute is a non-

electrolyte (M), or $\text{RX} \begin{array}{l} \text{H} \\ \text{OH} \end{array}$ and $\text{H}_2\text{O} \begin{array}{l} \text{R} \\ \text{X} \end{array}$ when the solute is an electrolyte (R^+X^-). As the concentration of the electrolyte

decreases, $\text{RX} \begin{array}{l} \text{H} \\ \text{OH} \end{array}$ is supposed to be converted into hydrinol,

$\text{H}_2\text{O} \begin{array}{l} \text{H} \\ \text{OH} \end{array}$, until ultimately the solution contains the solute only

in the form $\text{H}_2\text{O} \begin{array}{l} \text{R} \\ \text{X} \end{array}$ together with an equal number of molecules

of hydrinol. These "distributed" complexes are the active constituents of the system and have the power to attract single hydrones, thus serving to restore the hydrone equilibrium. The osmotic pressure is supposed to be due to these extra hydrone molecules, the latter being proportional to the number of "distributed complexes."

A theory similar to that of Armstrong has been presented by

Kling and Lassieur (53). The hydrol (Armstrong's "hydrone," and the simple H_2O molecule) is supposed to be a conductor of electricity while the polymers are not. This hydrol is believed to exist in two tautomeric forms, $\text{H}_2 = \text{O}$ and $\text{H}-\text{O}-\text{H}$, the first basic and the second acidic, $(\text{H}_2\text{O})_2$ being the neutralized product. When an acid is added, it is supposed to combine with $\text{H}_2 = \text{O}$. The ionic conception of hydrogen ion concentration is substituted by the concentration of the acid hydrol molecules.

Both of these theories are considered inadequate by Auger (54). If there is an equilibrium between $(\text{H}_2\text{O})_n$ and $n\text{H}_2\text{O}$, any hydrone that was fixed by a solute would be replaced by the equilibrium and as a consequence, the vapor pressure (supposed to be directly proportional to the concentration of hydrone) would not be lowered. His objection to the second theory is that there can be no equilibrium between the two tautomeric forms of hydrol or otherwise there would never be an excess of one form in solution.

Tammann (55) has recently contributed a paper on the molecular composition of water, reiterating that the fact that water reaches a minimum volume at 4° can be explained by the presence of molecules of greater volume, which increase in concentration as the temperature is decreased. This molecular form (Type 1) is supposed to have the same space lattice as ordinary ice and to exist at temperatures up to 50° and pressures between 0 and 2500 kgm. per square centimeter. Other forms of water molecules are supposed to be present in the liquid, but they are not so important in determining the physical properties. The degree of polymerization of this form has been determined from thermodynamic data to be either $(\text{H}_2\text{O})_9$, in which case it splits into $9(\text{H}_2\text{O})_1$, or $(\text{H}_2\text{O})_6$, in which case it divides into $2(\text{H}_2\text{O})_3$. The heats of dissociation and specific heats are estimated. The change in viscosity with temperature and pressure does not seem to be strictly dependent upon the concentration, but surface tension and index of refraction below 60° are proportional to the concentration of Type 1 molecules.

In a second paper Tammann (56) pointed out that the addition of a relatively nonvolatile substance (salts) displaces the volume minimum to lower temperatures, and decreases the compressi-

bility in the same manner as an increase of external pressure. These alterations were attributed to changes in molecular complexity of the water, to a decrease in the concentration of molecular Type 1. If a non electrolyte is present whose solubility increases with the amount of Type 1 (more soluble in cold water than in hot), then it will be less soluble in the salt solution. This idea was tested by solubility determinations.

X-RAY ANALYSIS OF LIQUID WATER

An entirely new method of studying liquids has come from the application of x-rays to the liquid state. When a liquid is substituted for the solid in a powder photograph experiment a very different diffraction effect is produced, the picture consisting of broad but distinct bands rather than sharp lines. The bands are similar to those produced by glassy solids. There is at present no agreement as to the source of these bands.

Debye and Scherrer (57) proposed that the bands arise from interference of rays scattered by the atoms within the chemical molecules of the liquid. Hewlett (58) assumed a crystal structure in the liquid state. On the other hand, Keesom and de Smedt (59) believed that the bands arise from rays scattered by molecules that are arranged in a more or less regular manner. On the assumption that the molecules are closely packed spheres, de Smedt (60) has calculated the degree of association of several organic liquids. Raman (61) does not agree with these conceptions but believes that the "liquid patterns" arise from regular differences in density existing in the liquid. An attempt has been made by Raman and Ramanathan (62) to calculate this regularity thermodynamically from the compressibility of the liquid.

A series of experiments by Wyckoff (63) on liquid mixtures shows that the pattern of a liquid mixture is the sum of the diffraction of its components and substantiates the conclusion that the origin of the pattern is within, rather than *between* molecules, although the results do not exclude the possibility of their arising from characteristic association of the molecules. Katz (64) has shown that the degree of polymerization of a solute does not affect the diameter of the diffraction ring, for such sub-

stances as rubber in isoprene, etc. Zernike and Prins (65) demonstrated to their satisfaction that the patterns cannot be due to arrangements of electrons in atoms or of atoms in molecules. Future work alone will give the true explanation of this property of liquids.

Langmuir (66) believes that a liquid resembles a solid in that there is no molecular unit of structure, but rather that the molecules are held together by chemical forces of the same character as the forces acting between atoms. Recently Daniels and Williams (67) and Antonoff (68) have published data on the specific heats of liquids which seem to show that this property is discontinuous. This is explained by probable changes in molecular complexity.

Latimer and Rodebush (69) have studied the structure of water from the electronic point of view and consider it to occupy an intermediate position between hydrogen chloride and ammonia. They suggest that a free pair of electrons on one molecule might be able to exert sufficient force on a hydrogen atom held by a pair of electrons on another molecule to bind the two molecules together. Such a union is not limited to the formation of double or triple molecules. This sort of association is very different from that of acetic acid (in which definite double molecules are supposed to be formed) and is probably the factor that produces the extremely high dielectric constant.

AGGREGATES IN EQUILIBRIUM

The hypothesis that liquid water contains various aggregates in equilibrium and that the equilibrium is changed by a second substance has found a number of applications within the past decade. In a very interesting paper by Richards and Palitzsch (70) it is shown that the solution volumes, viscosities, surface tensions and compressibilities of aqueous solutions of urethane can all be explained by assuming that the bulky trihydrol molecules (according to the theory of Bousfield and Lowry) are broken up as an effect of the solute. The compressibility curve, for example, shows a very decided minimum, the compressibility of the dilute solutions (up to about 25 per cent) being less than that

of pure water. The decrease is attributed to the effect of the solute on the solvent, the bulky polyhydrol molecules breaking up to form molecules having a smaller volume and compressibility, while the increase in the property at higher concentrations is attributed to the urethane possessing a greater compressibility than the dihydrol¹ which has increased in amount in the liquid as the concentration of urethane has increased.

Pagliani (71) has used the same explanation for solutions of alcohol and water, although the viscosities could not be explained as easily as the compressibilities.

The viscosities of certain dilute aqueous solutions are less than that of pure water at room temperatures. To this has been applied the misnomer of "negative viscosity." A few alcohol and glycerine solutions show the same behavior. Rabinovich (72) has made a critical study of the different factors acting upon the viscosity, particularly those factors which are able to lower the internal friction of the solvent. One of the most important of these factors is supposed to be the depolymerization of the associated solvent and it is this factor alone which is able to produce by itself negative viscosity. The simpler water molecules are supposed to have a viscosity very much smaller than the polyhydrol, so that the change in viscosity through a change in solvent more than offsets the increase due to the presence of a viscous solute.

POLYMERIZATION

Richards and Chadwell (73) contributed further evidence for the theory of the polymerization of water through a study of volume changes and compressibilities of aqueous solutions of non electrolytes. The results were explicable by reference to three causes: (a) the mutual affinity or attraction manifested by the liquids for one another in relation to the cohesive affinities of the pure liquids; (b) the effect of depolymerization of one or both liquids, and possible solvation; (c) the effect of the several compressibilities of the cohering substances.

¹ A possible structure for dihydrol is given by Anderegg, Proc. Indiana Acad. Sci. (1923), p. 93.

An illustration of the application of these considerations is of interest in our present discussion. It was found that the contractions taking place upon the formation of one liter of aqueous solutions of urethane, methyl acetate, and ethyl ether increased with an increase in concentration of the solute and for a given molal concentration was greater for ether than for methyl acetate, which in turn was greater than urethane. These three solutes are considered to be little associated.

They are, therefore, suitable for preliminary comparison. The average compressibilities (between 100 and 300 megabars) of these three substances in the liquid condition at 20° are, respectively, 132, 88 and about 46 (each $\times 10^{-6}$). Evidently, the contractions (15, 8 and 4.2 cc.) which take place on forming a solution containing one mole of solute per liter are roughly proportional to these compressibilities.

One might infer that the compressibility of the solute is the only factor in the volume change, but this inference would be superficial. It is not the compressibility of the solute alone which must be considered, but rather its relation to that of the solvent. Now the compressibility of liquid urethane is not far from that of water, although probably somewhat greater. If no other circumstance entered into the situation, liquid urethane ought to be nearly "isofluid" with water, involving no volume change on mixing. There is thus reason to believe that the rather large volume change which actually occurs when urethane is dissolved in water is primarily due not to further compression of urethane or water in the act of solution, but rather to some other circumstance, presumably the depolymerization of some of the water, which would cause a diminution in volume, since there can be little question that the more complex molecule of water is more bulky than a less complex molecule. This conclusion gives a clue which will be followed later as to the extent of polymerization of water. It does not, however, invalidate the conclusion that compressibility as indicated by the behavior of the solutions of ether, methyl acetate and urethane, is probably an essential factor in the volume change, the later being greater, the greater the compressibility of the solute. The same solvent is common to all.

The relative differences in contraction cannot be due to the effect of several affinities because, judging from the extent of solubility, ether has the least and urethane the greatest affinity of the three substances for water. This latter inference might also be drawn from the heats of

solution of similar substances in various solvents, determined by Speyers.

Turning now to a study of the effect of a single solute on different solvents, the changes in volume were determined for the solution of urethane in benzene, alcohol, water, and ether.

Again ether, the most compressible of all these solvents, gives by far the greatest change in volume. In the case of benzene the smaller compressibility (77×10^{-6}) and small affinity (shown by the slight solubility and great negative heat of solution) are presumably the reasons why this substance gives a slight *increase* rather than a decrease in volume. Alcohol and water behave as would be expected, taking account of their association; the volume change in the case of water is over twice as great as in the case of alcohol, although the compressibilities show the opposite relation. When urethane is dissolved in water, the dissociation of a part of the more complex molecules of water may be assumed to cause considerable contraction, and this contraction is to be added to that (if any) due to the mutual compression of the two substances. On the other hand, in the case of alcohol the dissociation (by causing expansion) would tend to decrease the volume change. Hence, the transposition of the two curves is only to be expected. The effect of change of polymerization may then be inferred (with regard to this particular pair) to exceed that due to the different compressibilities.

These qualitative considerations are inevitably incomplete, especially in view of the fact that the compressibilities of all substances diminish (to various extents) with increasing pressure. Nevertheless, they are not without significance.

No evidence as to the actual number of water molecules in the polyhydrol was found in these experiments, although an approximate estimate was made of 28 per cent of polymer present in water at 20°.

One of the most impressive pieces of evidence for the theory of the polymerization of water was found in the fact that the compressibilities of aqueous solutions of ether and methyl acetate are less than water, even though the compressibilities of the pure solute are very much greater. (The coefficient of compressibility of ether is about three times and that of methyl acetate two times

as great as that of water.) The half molal solutions of these solutes and urethane possess a compressibility about 3 per cent less than that of pure water. It appears that the compressibility of any dilute aqueous solution is less than that of water, and that the only plausible cause of this common effect is the depolymerization of water.

Since the viscosity of the depolymerized water molecules is supposed to be less than that of the polyhydrol, the viscosities of these aqueous solutions might be expected to be considerably lower than that of water. Chadwell has shown that this is not the case at a temperature of 25°, (74), but instead the viscosities of the solutions are greater. This increase in viscosity seems to be a general property of aqueous solutions of nonelectrolytes, at least at a temperature of 25°. The effect of the change in polymerization is covered up by other factors, possibly change in volume, etc.

Still another abnormal property that can be explained by the theory is the variation with temperature of the magnetization (75).

An entirely different application of the theory is the explanation of Bancroft (76) for the peptization of gelatin by various salt solutions. The addition of salt affecting the water equilibrium is supposed to affect the peptization if one of the forms of water is the determinant favoring peptization. One of Bancroft's students, Bowe (77), has used the theory in the study of the neutral salt effect.

The pertinence of the water equilibrium to phenomena related to aqueous solutions of electrolytes has been recognized by many investigators, but very little progress has been made in applying the ideas to the electrical properties of solutions. For instance, Kendall (78) has considered the consequences of a shift in equilibrium in an elucidation of the application of ideal solution equations to dilute aqueous solutions.

Bancroft (80) in reviewing the present status of the theory of electrolytic dissociation says:

Forty years of intensive development have brought us to the point where we cannot determine any electrolytic dissociation with any

degree of accuracy and where we question the significance of the term "electrolytic dissociation." . . . It is easy enough to point to one factor which has been neglected practically completely and which may be the one which has caused most—and perhaps all—of our difficulties. For years H. E. Armstrong in England has chided the physical chemists for considering water only as water, whereas it is a complex and variable mixture. This criticism seems well founded; but unfortunately, Armstrong has never succeeded in showing what could be done with his idea and consequently, the idea has been valueless hitherto. Everybody admits that water is a polymerized liquid and that the degree of polymerization may change on the addition of electrolytes. Sutherland, Lewis, McBain and others have suggested such a displacement of equilibrium as a possible source of error in our physical chemistry calculations; but nobody seems to have made a serious attempt to see how adequate this suggestion is.

Let us hope that in the near future rapid progress will be made in this important field of investigation.

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