

163. *The Influence of a Solvent on the Strength of the Hydrogen Bridge.*

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The distribution of acetic acid between benzene and water has been examined experimentally over wide temperature ranges, and at lower concentrations than in previous work.

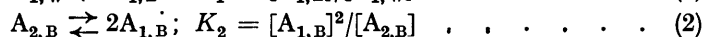
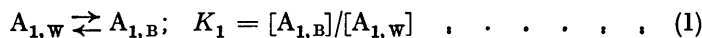
The increase in internal energy attending the dissociation of the double molecule in benzene solution is found to be some 5,400 cal. less than the corresponding value for the gaseous dissociation.

The difference in the two energies is quantitatively related to the distance apart of the polar solute molecules in combination, to the number and average distance of neighbouring solvent molecules round the dimer, and to the polarisability of the solvent molecules.

THE distribution of acetic acid between water and benzene has been investigated in order to discover what influence the inert solvent may exert on the energy of formation of a

typical hydrogen bridge. The procedure adopted differs sufficiently from the original treatment (Nernst, *Z. physikal. Chem.*, 1891, **8**, 110) to deserve a brief description.

Let the acetic acid molecule be denoted by A, and its monomeric and dimeric forms by the subscripts 1 and 2 respectively. The subscripts W and B refer to the solvents, water and benzene, respectively. The partial ionisation in aqueous solution can be neglected. We have then the following two equilibria to consider :



It follows that the ratio, c_B/c_W , of the total concentrations of acetic acid in the benzene and water layers is

$$\frac{c_B}{c_W} = K_1 + \frac{2K_1^2}{K_2} c_W \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The observed partition ratio should therefore increase linearly with the total concentration of solute in the aqueous layer. The intercept corresponding to a zero aqueous concentration yields the first equilibrium constant, and the gradient the second equilibrium constant.

These relations are found to be valid provided c_W does not exceed about 2 g.-mols./l. at the lower temperatures and about 0.8 at the higher temperatures. Most of the experiments have accordingly been made with aqueous solutions of acetic acid not exceeding the normal concentration. In this region, equation (3) leads to unambiguous values of the desired constants, K_1 and K_2 .

EXPERIMENTAL.

Distribution equilibrium was attained by vigorously shaking the two solvent layers with an appropriate amount of solute in glass-stoppered bottles under thermostatic equilibrium. 25 C.c. of the upper layer were titrated directly against standard alkali, phenolphthalein being used as indicator. The concentration of the aqueous layer was determined after dilution. The results of a typical experiment are shown in Table I; T_B and T_W are respectively the number of c.c. of 0.01835N-potassium hydroxide required to neutralise the acid in 25 c.c. of the benzene solution and 1 c.c. of the water solution. The concentrations, here and throughout, are given in g.-mols./l. The validity of equation (3) is demonstrated by the concordance of the figures in the last two columns.

TABLE I.

$$T = 297.23 \text{ }^\circ\text{K. } K_1 = 8.0 \times 10^{-3}. \quad K_2 = 5.6 \times 10^{-3}.$$

T_B .	T_W .	c_B .	c_W .	obs.	$100c_B/c_W$, by eqn. (3).
48.87	59.38	0.03586	1.0900	3.29	3.29
33.79	48.25	0.02480	0.8855	2.80	2.82
21.13	36.30	0.01551	0.6661	2.32	2.32
10.57	23.58	0.00776	0.4328	1.79	1.79
4.13	12.48	0.00303	0.2291	1.32	1.32

At higher temperatures, slight departures from the linear relation were found, due chiefly to loss of the volatile solute vapour from both layers during separation and analysis. A larger number of observations are therefore necessary, and, where some latitude remains in the choice of constants, the method of least squares has been used in determining both. A typical set of figures is shown in Table II. The second readings of each pair were made after the first, and

TABLE II.

$$T = 318.17 \text{ }^\circ\text{K. } K_1 = 1.39 \times 10^{-2}; \quad K_2 = 1.62 \times 10^{-3}.$$

c_B .	c_W .	$100c_B/c_W$.	$100c_B/c_W$, by eqn. (3).
0.00425 } 0.0042	0.2270 } 0.222	1.872 } 1.87	1.90
0.00406 } 0.0042	0.2166 } 0.222	1.876 } 1.87	1.90
0.01091 } 0.0109	0.4423 } 0.442	2.467 } 2.46	2.43
0.01086 } 0.0109	0.4423 } 0.442	2.456 } 2.46	2.43
0.01910 } 0.0192	0.6473 } 0.649	2.951 } 2.97	2.92
0.01938 } 0.0192	0.6500 } 0.649	2.982 } 2.97	2.92
0.02968 } 0.0294	0.8576 } 0.857	3.461 } 3.43	3.42
0.02908 } 0.0294	0.8566 } 0.857	3.395 } 3.43	3.42
0.04198 } 0.0415	1.0772 } 1.068	3.896 } 3.89	3.92
0.04105 } 0.0415	1.0595 } 1.068	3.874 } 3.89	3.92

indicate the loss of solute during the experiment, particularly from the benzene layer and from the more dilute solutions. In view of these irregularities, we have taken the mean of each pair of readings in applying the method of least squares. Certain other results are recorded in summarised form in Table III. They suffice to show the range of validity of equation (3), with

TABLE III.

$T = 290.14 \text{ }^\circ\text{K. } K_1 = 6.4 \times 10^{-3};$ $K_2 = 4.0 \times 10^{-3}.$			$T = 298.18 \text{ }^\circ\text{K. } K_1 = 8.2 \times 10^{-3};$ $K_2 = 6.0 \times 10^{-3}.$		
$c_w.$	obs.	by eqn. (3).	$c_w.$	obs.	by eqn. (3).
0.375	1.41	1.42	0.231	1.36	1.34
0.585	1.83	1.85	0.350	1.60	1.60
1.194	3.14	3.10	0.447	1.80	1.82
2.215	5.10	5.19	0.550	2.07	2.05
			1.140	3.38	3.375

$T = 307.82 \text{ }^\circ\text{K. } K_1 = 1.08 \times 10^{-2};$ $K_2 = 9.8 \times 10^{-3}.$			$T = 335.11 \text{ }^\circ\text{K. } K_1 = 2.055 \times 10^{-2};$ $K_2 = 3.61 \times 10^{-2}.$		
$c_w.$	obs.	by eqn. (3).	$c_w.$	obs.	by eqn. (3).
0.222	1.61	1.61	0.227	2.56	2.58
0.450	2.13	2.15	0.427	3.08	3.05
0.665	2.66	2.66	0.646	3.58	3.57
0.877	3.11	3.17	0.867	4.07	4.08
1.094	3.58	(3.68)			

respect to concentration and temperature. Experiments with ordinary benzene and with the purest *benzolum pro analysi* failed to reveal any difference in the value of either constant.

The influence of temperature on the equilibrium constants is adequately summarised by a relation of the form

$$K = e^{\Delta S^\circ/R} e^{-\Delta H^\circ/RT} \quad (4)$$

with the specific values

$$\Delta S_1^\circ = 7.15 \text{ cal./g.-mol.-deg.}; \quad \Delta H_1^\circ = 4980 \text{ cal./g.-mol.}$$

$$\Delta S_2^\circ = 22.32 \text{ cal./g.-mol.-deg.}; \quad \Delta H_2^\circ = 9700 \text{ cal./g.-mol.}$$

Experimental values and those reproduced by these formulæ are compared below. Because

$T, \text{ }^\circ\text{K.}$	$K_1 \times 10^3,$		$K_2 \times 10^3,$		$T, \text{ }^\circ\text{K.}$	$K_1 \times 10^3,$		$K_2 \times 10^3,$	
	obs.	by eqn. (4).	obs.	by eqn. (4).		obs.	by eqn. (4).	obs.	by eqn. (4).
290.14	6.4	6.51	4.0	3.73	307.82	10.8	10.64	9.8	9.77
297.23	8.0	7.98	5.6	5.57	318.17	13.9	13.86	16.2	16.4
298.18	8.2	8.18	6.0	5.88	335.11	20.6	20.68	36.1	35.7
303.56	9.5	9.50	7.8	7.85					

the dissociation in solution is attended by a negligible change in volume, we may identify ΔH_2° with ΔE_s° , which is the increase in internal energy for the dissociation in solution. The corresponding value for the gas reaction, ΔE_g° , has been variously given as 14,200 cal. (Nernst, "Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes," Halle, 1918) and 16,000 (Eucken, "Grundriss der physikalischen Chemie," 4th Ed., Leipzig, 1934). Taking a mean value, we have the ratio

$$\Delta E_s^\circ/\Delta E_g^\circ = 9,700/15,100 = 0.64 \pm 0.04 \quad (5)$$

and the difference

$$\Delta E_g^\circ - \Delta E_s^\circ = 5,400 \pm 900 \text{ cal./g.-mol.} \quad (6)$$

It is not possible to say how the increase of internal energy associated with the reaction in solution is affected by the small amount of water which inevitably enters the organic solvent in distribution equilibria. We shall assume that the solvent is essentially pure. At the mean temperature of experiment (313 °K.), its dielectric constant is 2.243.

DISCUSSION.

The origin of the type of association due to the hydrogen bridge is generally traced to the phenomenon of resonance (Pauling, "Nature of the Chemical Bond," Cornell, 1939). It has, nevertheless, been pointed out that classical electrostatics is also capable of explaining the facts. If we consider, for example, the coupling of two formic acid molecules into a

stable bimolecular complex in the gaseous phase, we can show that the interaction of the four polar components, summed vectorially, accounts for a dissociation energy of 13,140 cal., which is 93% of the observed effect (Moelwyn-Hughes, J., 1938, 1243). The superposition of the secondary effects due to polarisation and induction slightly improves the calculation, yielding a value of 13,440 cal., or 95% of the total effect (Davies, *Trans. Faraday Soc.*, 1940, **36**, 342). In view of the fact that the observed value relates to a temperature some 300° higher than that to which the calculation refers, the electrostatic theory may be regarded as wholly capable of interpreting the facts. For these reasons, only the classical electrostatic theory is here employed in discussing the new results.

(1) Solvents are known to modify the dipole moments of molecules which they dissolve, and the most obvious way of explaining the ratio of equation (5) would then be to attribute the stability of the dimer in the two phases entirely to the interaction of the monomeric dipoles. Provided the inclination and separation of the component molecules be the same in both phases, one would then have the approximate relation

$$\Delta E_s^0/\Delta E_g^0 \doteq (\mu_s/\mu_g)^2 \quad \dots \quad (7)$$

If such a simple explanation were true, the experimental ratio of the energy terms yields the result, $\mu_s = 1.38 \times 10^{-18}$ e.s.u., assuming $\mu_g = 1.73 \times 10^{-18}$ (Zahn, *Physical Rev.*, 1931, **38**, 521). Examination of the literature shows that there is much uncertainty about the true value of μ_s . All estimates agree that it is less than μ_g ; Briegleb's computation leads to a value of 1.04×10^{-18} e.s.u. (*Z. physikal. Chem.*, 1930, **B**, **10**, 220). Measurements of the polarity of solutions of acetic acid in benzene solution, however, have generally been made at concentrations so great that the equilibrium expression (2) does not retain its validity. Quite apart from such uncertainties, which are more fully discussed later, we consider that equation (7) is too simple an explanation.

(2) The two molecules which form the dimer are, of course, surrounded by solvent molecules, upon which each exerts some polarising influence. The effect is to diminish the effective field due to the dipole in the approximate ratio of $(D + 2)/3D$ (Frank, *Proc. Roy. Soc.*, 1935, **A**, **152**, 174). For the system under discussion, this leads to the result:

$$\Delta E_s^0/\Delta E_g^0 = (D + 2)/3D = 0.63 \quad \dots \quad (8)$$

Numerically, this ratio is quite satisfactory. The molecular model adopted in the calculation is, however, too simple to fit the experimental system; and we consider the following explanation to be, though still approximate, nearer the mark.

(3) On account of the symmetry of the plane six-membered ring formed by the dimeric modification of the acid in solution, we shall assume that its true energy of dissociation is the same in the condensed and the rarefied phase. The recorded difference is an apparent one, due to the difference in the standard states to which the two values of ΔE^0 refer. ΔE^0 is, in fact, a measure, not of the energy of the hydrogen linkage, but of the difference between the molar internal energies of two molecules of the monomeric acid and one molecule of the dimeric acid, each in the reference state. Denoting solution values by s and gas values by g , we then have, for dissociation at the absolute zero:

$$\Delta E_{0,g}^0/N_0 = 2\mu_g^2 \cos^2 \theta_s/r_g^3 \quad \dots \quad (9)$$

and

$$\Delta E_{0,s}^0/N_0 = 2u_i + 2\mu_s^2 \cos^2 \theta_s/r_s^3 \quad \dots \quad (10)$$

N_0 is the Avogadro number. The common reference level is that of zero energy for the isolated monomeric molecules in the dilute gaseous phase. The term u_i is the potential energy of a single molecule in the supercooled solution. In order to estimate its magnitude, we shall ignore the work done in forming the cavity in the solvent, as this is counterbalanced by the corresponding term for the dimer. The field exerted by the solute molecule, of moment μ_s , at a distance r in its neighbourhood is

$$F_s = \mu_s(1 + 3 \cos^2 \theta)/r^3 \quad \dots \quad (11)$$

If the solute is free to rotate in an envelope of n solvent molecules, of polarisability α , the solute-solvent interaction energy is

$$u_i = -\frac{1}{2}n\alpha F_s^2 \quad \dots \quad (12)$$

which has an average value of

$$u_i = -n\alpha\mu_s^2/r^6 \quad \dots \dots \dots (13)$$

According to our supposition, we regard $\mu_s = \mu_g$, $r_s = r_g$, and $\theta_s = \theta_g$, so that

$$\Delta E_{0,g}^0 - \Delta E_{0,s}^0 = -2N_0 u_i = 2N_0 n\alpha\mu_s^2/r^6 \quad \dots \dots \dots (14)$$

and, for a linear combination of the dipoles,

$$E_{0,s}^0/E_{0,g}^0 = 1 - n\alpha r_s^3/r^6 \quad \dots \dots \dots (15)$$

An independent check on these suppositions would be possible from distribution measurements of the solute between the solvent and the vapour phase; but figures at sufficiently low concentrations seem to be lacking. We can therefore but equate the experimental and theoretical relations (6) and (14), obtaining $r = 3.39 \text{ \AA}$. ($n = 6$) and $r = 3.82 \text{ \AA}$. ($n = 12$). In view of the approximations made, these figures are reasonable ones.

Remarks on the Polar Constants of Associating Solutes.—It is the object of this section to show how many of the apparent anomalies recorded in connexion with the partial molar polarisation of associating solutes disappear when allowance is made in a quantitative manner for the extent of association. We have noted that most of the data for associating solutes have been computed on the basis that dimerisation is complete.

We may consider, as an example, the case of acetic acid dissolved in benzene. The assumption of complete association drives Briegleb (*loc. cit.*) to the further assumption that higher polymers are also formed. Smyth and Rogers (*J. Amer. Chem. Soc.*, 1930, 52, 1824) rightly attribute the anomalous temperature variation of the partial molar polarisation of the solute to the inaccuracy of their assumption of complete association. Extrapolating at each temperature from data relating to solutions of various molar fractions, they arrive at the figures reproduced in lines 1 and 2 of the following table. In

$t^\circ \text{ C.}$	0	10	20	30	40	50	60	70
P_∞ (c.c./g.-mol.)	21.3	22.4	22.8	23.1	23.7	24.2	24.8	25.5
$K_2 \times 10^3$	1.31	2.46	4.42	7.64	12.76	20.75	32.66	50.12
Percentage of total acid present in monomeric form in 1M-solution.	2.53	3.45	4.59	5.99	7.67	9.62	11.97	14.63

terms of the equilibrium constant of equation (2), the fraction of the total concentration of solute which is associated into double molecules is given by the equation

$$x/c_B = 1 + K_2/4c_B - \{(1 + K_2/4c_B)^2 - 1\}^{1/2} \quad \dots \dots \dots (16)$$

In line 3 are found the equilibrium constants for dissociation, obtained by means of equation (4); and in the last line are the fractions of free solute molecules, expressed as a percentage, in a solution of 1M-concentration. Denoting by P_1 the molar polarisation of the dissolved monomer, and by P_2 the corresponding quantity for the dimer, we then have the relation

$$P_\infty = P_1(1 - x) + P_2x \quad \dots \dots \dots (17)$$

where, according to Debye's theory,

$$P_1 = a + b/T \quad \dots \dots \dots (18)$$

Combining, we obtain the result

$$(P_\infty - P_2x)/(1 - x) = a + b/T \quad \dots \dots \dots (19)$$

In order to solve the equation, we have assumed that P_2 equals the molar refraction of solid acetic acid (19.4 c.c./g.-mol.). Computing from the extreme points in the foregoing table, we thus deduce that $\mu_s = 2.71 \times 10^{-18}$ e.s.u. The result is, of course, too high, because we have used the extents of dissociation in M-solutions, which are less than those in the dilute region to which the extrapolated values refer. The significant result, however, is that the temperature dependence of the polarisation is now correct. It is because the value of μ_s estimated here lies as far above μ_g as the values of μ_s estimated elsewhere lie below it that we have had to assume no real change in the dipole moment on dissolution.

Other Association Equilibria in Solution.—The method of this paper has not, apparently, been used in the study of equilibria. Accordingly, we append some other values of K_2 obtained by this method from some of the earlier data to be found in the literature. The figures in Table IV have been obtained by the linear graphical procedure, and refer to

TABLE IV.

Solute.	Solvent.	$K_2 \times 10^3$.	Author.
$\text{CH}_3 \cdot \text{CO}_2\text{H}$	CS_2	2.35	Herz and Kurzer, <i>Z. Elektrochem.</i> , 1910, 16 , 869.
$\text{CH}_3 \cdot \text{CO}_2\text{H}$	C_6H_6	6.0	Moelwyn-Hughes.
$\text{CH}_3 \cdot \text{CO}_2\text{H}$	CCl_4	6.1	Herz and Kurzer, <i>loc. cit.</i>
$\text{CH}_3 \cdot \text{CO}_2\text{H}$	CHCl_3	143	Rothmund and Wilsmore, <i>Z. physikal. Chem.</i> , 1902, 40 , 611.
$\text{C}_6\text{H}_5 \cdot \text{CO}_2\text{H}$	C_6H_6 (20°)	5.70	Nernst, <i>loc. cit.</i>

systems at 25°, the other solvent being water. The last value is probably more accurate than the others. The plot falls through ten points in a concentration range below 0.016 g.-mol./l.

We have tested equation (3) also for the distribution of solutes between associating and non-associating solvents in the absence of the hydrogen bridge, and have found it to apply generally.

The distribution law involving only dimerisation is usually stated in the simplified form given to it by Nernst, who initiated the study of the present problem. In its early form, it assumes complete association, and is expressed as

$$\sqrt{c_B}/c_W = K \quad (20)$$

It is clear that the present form of the law is more general, and that it reduces at high concentrations into the simpler one, when

$$K = K_1\sqrt{2/K_2} \quad (21)$$