559. *Solutions of Alcohols in Non-polar Solvents. Part I. The Solubility and Heat of Solution of Water in Dilute Solutions of Alcohols in Benzene.*

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The solubility of water in dilute solutions of methanol, ethanol, *n*-butanol, *n*-pentanol, and *n*-octanol in benzene has been determined by the synthetic method over a range of temperature. An apparatus is described with which the three components can be introduced into a tube so that the amount of each is known with considerable precision, even though that of the water is very small. The molar heat of solution of water ΔH has been evaluated from the solubility results. Whereas ΔH for benzene solutions of pentanol and octanol decreases with increasing alcohol concentration, with butanol solutions ΔH first rises slightly before undergoing a fairly rapid fall. This peculiar course of ΔH at low alcohol concentrations is ascribed to an interaction between the alcoholic hydroxyl group and the polarisable benzene molecules which in turn affects that between the water and benzene. It is suggested that the reason for the different behaviour of the pentanol and octanol solutions is that the molecules of these alcohols tend to adopt a coiled configuration in benzene, whereby the hydroxyl group is partly screened. For dilute solutions of butanol, pentanol, and octanol in benzene, there is a linear relation between the heat and entropy of solution of water.

In a previous paper (Staveley, Jeffes, and Moy, *Trans. Faraday Soc.*, 1943, **39**, 5) some measurements of the solubility of water in benzene containing organic substances of various chemical types were reported. These measurements were intended to throw light on the interaction between molecules of water and those of the organic substances. It seemed that a useful extension of this work would be to examine in greater detail the solubility of water in benzene solutions of substances such as simple alcohols with which water molecules interact particularly strongly. Previous studies of three-component systems involving water, an alcohol, and a non-polar solvent have usually been carried out at one temperature only, and in any case have not been sufficiently detailed at low alcohol concentrations to give any information about the interaction of *monomeric* alcohol and water molecules.

From measurements of the solubility of water in a given medium over a range of temperature an estimate can be made of ΔH, the heat of solution of water. (The basis of this calculation will be discussed more fully later.) Before the experiments were commenced, it was expected that the addition of alcohol to benzene would decrease ΔH, owing to the exothermic interaction of water and alcohol molecules, and it was hoped to estimate the heat of this interaction from the experimental curve relating ΔH and alcohol concentration. Experiments were therefore carried out on the solubility of water in benzene solutions of methanol and ethanol, using the simple technique employed in the earlier work. (This consists in sealing within a tube a small known amount of water with a known amount of the organic medium, heating the tube until the contents become homogeneous, and then finding the temperature at which the aqueous phase appears on cooling). The results were surprising, in that, as the alcohol concentration increased from zero, ΔH did not at first show its expected fall, but instead remained almost constant or even rose slightly to a maximum value, after which there was a rapid drop. One objection to these experiments, however, was that the aqueous phase which separates from even very dilute solutions of methanol or ethanol in benzene is not pure water, but contains considerable quantities of the alcohol. It was therefore considered desirable to carry out further experiments with higher alcohols, and this was done with *n*-butanol, *n*-pentanol, and *n*-octanol.

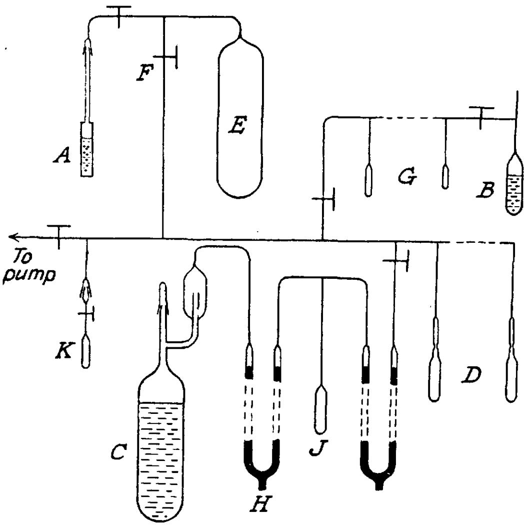
Values for the solubility of water in benzene have recently been obtained by Joris and Taylor (*J. Chem. Physics*, **1948**, **16**, 45) using tritium. These are considerably lower than those obtained by both synthetic and analytical methods, and Joris and Taylor suggest possible reasons why the latter methods might lead to erroneously high values. It seems curious, however, that their value for the solubility of water in benzene at 20° is even lower than the concentration of water in benzene in equilibrium with the salts Na_2SO_4 and $Na_2SO_4,10H_2O$. In the determination of the latter quantity (Bell, *J.*, 1932, 2903) the analytical method used had been very carefully tested, and interference from colloidally dispersed water (which Joris and Taylor suggest as a possible source of error in the synthetic method) can scarcely arise. It seems to us that it cannot be regarded as proven that the synthetic method does not give reliable results when applied to systems of this kind.

EXPERIMENTAL.

Any one solubility determination involved making up a mixture of known amounts of water, benzene, and the alcohol in a sealed tube, heating this until it became homogeneous, and then determining the temperature at which the system separated into two phases on cooling. This temperature could be determined to 0·1—0·2°. In the experiments on methanol and ethanol, the water was added from a weight pipette. The risk of loss by evaporation during this operation, the possibility of the benzene–alcohol mixture picking up atmospheric moisture during the transference of this mixture into the tube, and the fact that the quantities of water involved were very small, combined to make uncertainty in the exact mass of water sealed within a tube the chief source of experimental error.

FIG. 1.

Apparatus for filling tubes with known amounts of water, benzene, and an alcohol.



For the experiments on butanol and pentanol an improved technique was therefore adopted. All three components were manipulated in a closed apparatus and introduced into a tube by condensation in such a way that the amount of each was accurately known. For octanol, which is comparatively involatile, this method was used in a modified form, as described later.

Fig. 1 shows the main features of the apparatus used in the experiments with butanol and pentanol. The water was contained in the small copper vessel *A*, the alcohol in *B*, and the benzene in *C*. Each liquid was degassed by repeated freezing, evacuation, and melting. The tubes *D* into which the three substances were condensed were provided with constrictions at which they were eventually sealed off. The volume of each tube up to the mid-point of the constriction was determined in advance, and was ~30 c.c.

The volume of the vessel *E* (~470 c.c.) was such that when it was filled with water vapour at the vapour pressure of water at ~12°, the amount of water in it was the minimum required for any one of the tubes *D*. The actual quantity of water contained in *E* for a known pressure and with *E* at a known temperature (~25°) was found as follows : *A* was surrounded by water in a Dewar vessel and its temperature kept constant somewhere between 11·5° and 12·5°. After *E* had been evacuated, it was put in communication with the water in *A*. The temperature of *A* was read to 0·01°, and that of the bath surrounding *E* to 0·1°, and the communicating tap closed. By opening tap *F*, the vapour in *E* was condensed into the detachable trap *K*, which was cooled in liquid air. A period of 8 minutes was allowed for this condensation, this being more than sufficient for the pressure to fall below the minimum necessary for the production of a glow in a discharge tube. At the end of this time, F was closed and the whole process repeated until it had been carried out twenty times in all. The trap K, which now contained about 0·1 g. of water, was detached and weighed. The mass of water in E at each filling was then calculated on the assumption that the water vapour obeyed the perfect-gas laws, its pressure being the water vapour pressure at the temperature of A during the filling. The actual mass of water in the trap proved to be 1·014 times that obtained by summing the calculated values for each of the twenty fillings. Two repetitions of this calibration exeriment, also of twenty fillings each, gave exactly the same numerical factor. In preliminary experiments, it had been found that if the temperature difference between A and E was only 2—3°, the numerical factor was much larger and no longer reproducible, presumably owing to adsorption effects becoming considerable when the pressure of the vapour in E was only slightly less than the water vapour pressure at the temperature of E (cf. McHaffie and Lenher, *J.*, 1925, **127**, 1559). In introducing water into the tubes D in the same way, the temperatures of A and E were kept between the same limits as during the calibration experiments, and the sum of the calculated quantities of water for each filling was multiplied by the factor 1·014 to give the mass actually condensed into the tube. The number of fillings of E for any one tube D was of course chosen to give as nearly as possible the required total amount of water.

The capacities of the six small vessels G, of which two are shown, varied from 0·19 to 2·5 c.c. Each had a capillary inlet, and had been accurately calibrated at 0° to a mark on the capillary. In filling the tubes D for determinations of the solubility of water in a particular solution of an alcohol in benzene, the same vessel G was of course used throughout. Alcohol was condensed into it up to the calibration mark while it was surrounded by melting ice. The contents of the vessel were then condensed into the tube D.

Benzene was stored over phosphoric oxide in the vessel C. A mercury cut-off H separated it from a calibrated vessel J, the volume of which to a mark on the stem (~23 c.c.) had been found at a temperature just above the m. p. of benzene. J was maintained at this temperature when it was filled with benzene by evaporation from C, and this charge of benzene was then condensed into a tube D. The order of admission of the three substances into a tube was water, alcohol, benzene. The tube was finally cooled in liquid air and sealed off at the constriction. It is considered that the errors in the amounts of each of the three substances in a tube did not exceed 0·2%.

Octanol is too involatile to be transferred readily from one vessel to another by evaporation at ordinary temperatures. In the experiments with this substance, therefore, the required amount of water was introduced into a tube as described above. This was then filled with dry air to atmospheric pressure, and while still very cold was cut off the vacuum line above the constriction. The required amount of the octanol–benzene solution was siphoned into it, and the tube sealed off.

Accurate determination of the temperature at which the contents of a tube separated into two phases on cooling was assisted by focusing a powerful beam of light on the tube at right angles to the direction of observation, and by using a comparison tube filled with dry benzene.

Since it is known that considerable quantities of water vapour are adsorbed on glass when the pressure is near the saturation vapour pressure, it seemed desirable to investigate the possibility that as a tube is cooled appreciable quantities of water are adsorbed on the walls in the neighbourhood of the temperature at which the aqueous phase appears. If this happened it might, of course, introduce serious errors. Accordingly, several experiments were carried out in which, after the critical solution

TABLE I.

Solubility of water in benzene and in alcohol–benzene mixtures.

The solubility of water at t° is given as N, where N = mole-fraction of water × 10^3; $N_{\rm A}$ is the mole-fraction of alcohol; a and b are the values of the constants in the equation $\log_{10} N = a - 10^3 b/(t + 273{\cdot}1)$.

Benzene: a = 5·237; b = 1·427.

N	2·606	3·674	3·784	5·041	5·153	6·064	6·902	7·078
t	22·7°	30·5°	33·0°	40·6°	41·9°	45·9°	51·9°	52·2°
N	7·211	7·521	9·294	10·50	11·21	13·02		
t	53·2°	54·7°	60·9°	65·3°	67·2°	73·2°		

Methanol–benzene.

$N_{\rm A}$ = 0·0113; a = 5·219, b = 1·416.

N	3·07	3·96	4·62	6·18	9·455
t	26·0°	33·5°	37·7°	46·1°	60·1°

$N_{\rm A}$ = 0·0226; a = 5·339, b = 1·430.

N	2·88	4·51	6·21	8·87	9·80
t	20·0°	32·4°	42·0°	49·8°	56·4°

$N_{\rm A}$ = 0·0332; a = 5·158, b = 1·370.

N	4·15	5·08	6·08	7·77	10·18
t	28·7°	34·5°	40·1°	47·9°	56·5°

$N_{\rm A}$ = 0·04125; a = 5·217, b = 1·385.

N	4·26	4·675	7·375	9·07	12·23
t	28·4°	32·2°	44·6°	52·0°	62·8°

$N_{\rm A}$ = 0·0458; a = 4·935, b = 1·277.

N	4·07	7·44	9·17	14·11	15·09
t	22·5°	41·1°	47·4°	64·1°	67·6°

$N_{\rm A}$ = 0·0568; a = 4·358, b = 1·055.

N	6·41	7·89	9·31	11·71	12·51
t	23·7°	31·6°	37·9°	47·8°	50·7°

$N_{\rm A}$ = 0·0781; a = 3·704, b = 0·8208.

N	8·28	10·63	13·48	15·31	18·16
t	22·2°	32·7°	46·2°	53·1°	61·6°

$N_{\rm A}$ = 0·1047; a = 3·594, b = 0·7539.

N	9·44	10·82	14·63	16·45
t	15·0°	22·2°	35·6°	43·7°

TABLE I.—(*continued*).

Ethanol–benzene.

N_A = 0·00644; a = 5·638, b = 1·547.

N	3·12	3·96	5·29	8·02	8·51	12·19
t	27·2°	34·4°	42·2°	53·7°	55·2°	66·5°

N_A = 0·0143; a = 5·758, b = 1·571.

N	2·01	4·10	5·02	6·97	8·32	14·28
t	14·7°	32·6°	37·4°	46·4°	51·6°	68·7°

N_A = 0·0183; a = 5·341, b = 1·436.

N	3·42	5·555	6·91	8·27	10·87	13·06
t	26·1°	39·1°	45·4°	51·6°	60·6°	67·7°

N_A = 0·02465; a = 4·238, b = 1·070.

N	3·58	4·19	4·68	5·57	7·10	9·59	11·26	12·75
t	18·7°	23·1°	26·6°	32·1°	41·6°	57·3°	61·7°	68·4°

N_A = 0·02986; a = 3·323, b = 0·757.

N	4·71	7·01	8·38	10·53
t	16·7°	32·3°	43·4°	55·6°

N_A = 0·0563; a = 3·560, b = 0·765.

N	5·89	7·75	10·13	14·77
t	1·3°	12·2°	27·5°	48·6°

N_A = 0·04213; a = 3·397, b = 0·749.

N	5·96	8·27	9·62	9·70	10·04	14·62
t	11·5°	27·9°	38·6°	38·8°	39·0°	62·1°

N_A = 0·0691; a = 3·426, b = 0·702.

N	9·30	11·12	13·57	16·60	19·43
t	13·0°	21·4°	32·6°	41·6°	56·5°

Butanol–benzene.

N_A = 0·00802; a = 5·342, b = 1·439.

N	3·272	4·345	6·027	8·224
t	24·7°	32·6°	42·3°	51·5°

N_A = 0·0329; a = 3·121, b = 0·681.

N	5·755	7·082	8·065	9·745	11·80
t	14·8°	26·4°	34·3°	45·9°	57·9°

N_A = 0·01405; a = 4·745, b = 1·221.

N	3·366	6·209	8·056	10·38
t	16·8°	35·6°	45·1°	54·2°

N_A = 0·0561; a = 2·807, b = 0·545.

N	7·949	9·380	11·01	12·67	14·67
t	12·6°	24·1°	35·9°	47·2°	60·2°

N_A = 0·02615; a = 3·585, b = 0·845.

N	4·665	5·746	6·968	8·511	10·27
t	18·8°	26·8°	35·0°	44·0°	51·9°

N_A = 0·0973; a = 2·763, b = 0·479.

N	12·30	14·19	16·25	18·37	20·97
t	13·8°	24·3°	35·6°	46·8°	59·5°

Pentanol–benzene.

N_A = 0·00698; a = 4·948, b = 1·310.

N	2·690	3·803	5·429	7·418	10·01
t	17·2°	27·8°	38·0°	48·2°	57·8°

N_A = 0·0119; a = 4·780, b = 1·238.

N	2·926	3·394	3·927	5·095	5·928	7·063	9·036	11·08
t	12·8°	17·9°	22·7°	31·7°	36·3°	41·9°	49·6°	56·7°

N_A = 0·0223; a = 4·292, b = 1·076.

N	3·803	3·837	4·839	5·794	6·798	6·947	8·802	11·58
t	15·0°	15·4°	23·2°	30·4°	37·6°	37·9°	47·3°	58·3°

N_A = 0·0281; a = 2·838, b = 0·603.

N	5·766	5·853	6·968	7·841	8·851	9·851
t	16·7°	17·4°	29·0°	37·4°	45·0°	51·8°

N_A = 0·0486; a = 2·771, b = 0·546.

N	7·814	9·414	11·21	12·75	14·94
t	18·1°	31·2°	43·1°	52·0°	68·0°

N_A = 0·08425; a = 2·733, b = 0·480.

N	10·79	13·52	16·09	18·90
t	11·2°	28·4°	43·3°	57·8°

Octanol–benzene.

N_A = 0·0166; a = 4·613, b = 1·231.

N	2·735	3·735	4·355	6·284	8·556
t	22·5°	31·0°	33·0°	49·5°	62·1°

N_A = 0·0314; a = 4·137, b = 1·030.

N	3·593	4·521	5·352	7·200
t	14·3°	23·7°	28·4°	41·65°

N_A = 0·0435; a = 4·217, b = 1·037.

N	5·699	6·621	7·258	7·952	9·348	11·05
t	26·0°	33·5°	35·8°	38·9°	46·7°	53·4°

temperature for a tube had been determined, the tube was warmed to a slightly higher temperature, opened, and the major part of its contents blown over into another dry tube. This was then sealed and used for another determination of the critical solution temperature. This temperature was always identical within the limits of experimental error (±0·2°) with that obtained with the first tube.

Benzene was chemically purified by the method of Richards and Shipley (*J. Amer. Chem. Soc.*, 1914, **36**, 1825; 1919, **41**, 2007), and then submitted to fractional crystallisation, or distillation, or both. It was finally dried over resublimed phosphoric anhydride. The alcohols were purified by fractional distillation, the butanol being first subjected to the chemical treatment described by Weissberger and Proskauer ("Organic Solvents," Oxford, 1935). They were dried first by refluxing them over freshly-ignited lime, and finally by means of aluminium amalgam (for butanol, pentanol, and octanol), or with magnesium (for methanol and ethanol).

Results.—In every solubility determination, a correction was applied for the amount of water present in the vapour phase in the tube. Values for the solubility of water in benzene and in various solutions in benzene of the five alcohols studied are recorded in Table I; N is the millimole-fraction of the water in a saturated solution at $t°$. In a series of experiments with solutions containing a fixed alcohol : benzene ratio, the mole-fraction of alcohol in the water-saturated solution decreases slightly as the temperature rises, owing to the increased solubility of water. As the change seldom exceeds 0·5%, the concentration of the alcohol in any one series has been given in Table I as a mean mole-fraction, N_A.

FIG. 2.

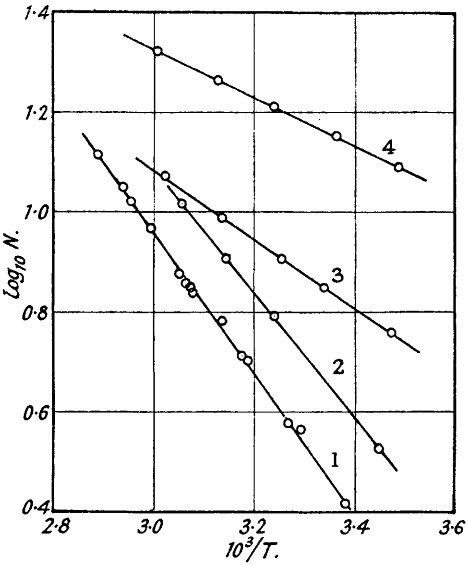


FIG. 3.

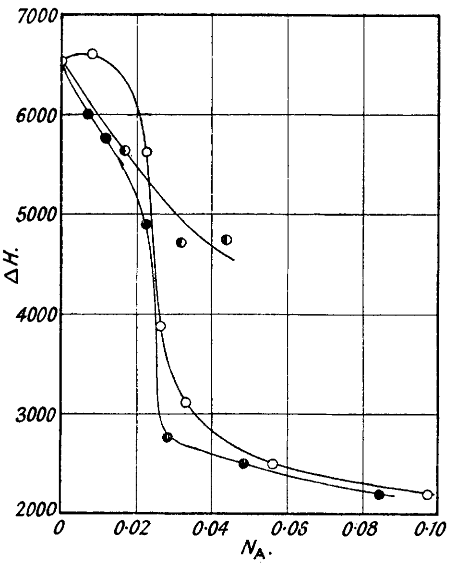


FIG. 2.

Specimen plots of $\log_{10}$ N *against* 10^3/T *for benzene and butanol–benzene mixtures.* (N *is the mole-fraction of water* × 10^3, *and* T *the absolute temperature*). *Line* 1 *is for benzene, and lines* 2, 3, *and* 4 *for butanol–benzene solutions containing the alcohol at mean mole-fractions of* 0·01405, 0·0329, *and* 0·0973, *respectively.*

FIG. 3.

Plots of ΔH (*in cals./mole, as calculated from equation* 2) *against* N_A, *the mole-fraction of alcohol, for butanol* (*open circles*), *pentanol* (*full circles*), *and octanol solutions* (*half-shaded circles*).

For benzene alone, and for every solution studied, log N is a linear function of $1/T$, where T is the absolute temperature. In Table I are recorded the values of a and b in the equation

$$\log_{10} N = a - 10^3 b/T$$

which were obtained from the experimental points by the method of least squares. How well this linear relation is obeyed is evident from Fig. 2, in which $\log_{10} N$ is plotted against $10^3/T$ for benzene alone and for several solutions of butanol in benzene.

DISCUSSION.

The temperature variation of the solubility of a non-ideal solute is governed by the exact equation

$$\Delta H = \boldsymbol{R}T^2\left(\frac{\mathrm{d}N}{\mathrm{d}T}\right)_{\text{sat.}}\left[\left(\frac{\partial \ln f}{\partial N}\right)_T + \left(\frac{1}{N}\right)_{\text{sat.}}\right] \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(cf. Williamson, *Trans. Faraday Soc.*, 1944, **40**, 421); ΔH is the heat absorbed when one mole of solute dissolves in an infinite amount of the saturated solution, and f and N are respectively the activity coefficient and mole-fraction of the solute. For solutions of water in benzene, Peterson and Rodebush (*J. Physical Chem.*, 1928, **32**, 709) found that the freezing-point depression is a linear function of the water concentration, the water being unimolecular up to the saturation limit, and Greer (*J. Amer. Chem. Soc.*, 1930, **52**, 4191) observed that, at 20·9°, solutions of water in benzene obey Henry's law with considerable precision. We may therefore regard the water in solution in benzene as an ideal solute and neglect the first term in the square bracket of equation (1), which accordingly simplifies to

$$\Delta H = \boldsymbol{R}T^2\left(\frac{\mathrm{d}\ln N}{\mathrm{d}T}\right)_{\text{sat.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

We shall suppose that equation (2) also applies to solutions of water in the mixtures of benzene and an alcohol. This assumes that the aqueous phase which separates from such mixtures is pure water, whereas it will in fact contain some of the alcohol. Some information about the composition of the aqueous phase can be obtained from the work of Butler and Harrower (*Trans. Faraday Soc.*, 1937, **33**, 171), who determined the limiting values of the distribution coefficients of the lower alcohols between water and benzene. From their figure for butanol, the mole-fraction of this alcohol in the aqueous phase in equilibrium with our most concentrated butanol–benzene solution should not exceed 0·028 at 25°, so the aqueous phase is at least 97·2 moles % water. Since, for the lower alcohols, the distribution coefficient rapidly increases with increasing molecular weight (in favour of concentration in the benzene), we may expect that for octanol and pentanol at the same concentration the water content of the aqueous phase is considerably nearer 100%. For the mixtures of benzene with butanol, pentanol, and octanol, the ΔH values recorded in Table II, which have been obtained by applying equation (2) to our solubility results, should therefore be very near the true values of the molar heat of solution of pure water. For methanol and ethanol the position is rather different. From Butler and Harrower's figures, the aqueous phase in equilibrium with a benzene solution containing one of these alcohols at a mole-fraction of only 0·01 is ~86 moles % water for methanol and ~95·5 for ethanol. Nevertheless, estimates of ΔH made by using equation (2) in the same way are also included in Table II, and it is noteworthy that they follow much the same course as those for the butanol solutions, in that, as the alcohol concentration increases from zero, ΔH first remains fairly constant, or even rises slightly, before undergoing a rapid fall.

TABLE II.

Values of ΔH, *in cals./mole, calculated from equation* (2) *for water in alcohol–benzene mixtures.*

[N_A is the mole-fraction of the alcohol. For water in benzene alone, ΔH = 6530.]

Methanol–benzene.

10^4N_A	113	226	332	412·5	458	568	781	1047
ΔH	6470	6540	6265	6330	5840	4825	3750	3450

Ethanol–benzene.

10^4N_A	64·4	143	183	246·5	298	421·3	563	691
ΔH	7040	7190	6570	4900	3465	3425	3500	3210

Butanol–benzene.

10^4N_A	80·2	140·5	261·5	329	561	973
ΔH	6600	5585	3875	3120	2500	2200

Pentanol–benzene.

10^4N_A	69·8	119	223	281	586	842·5
ΔH	6000	5760	4900	2770	2500	2200

Octanol–benzene.

10^4N_A	166	314	435
ΔH	5630	4710	4740

The systems water–methanol or ethanol–benzene could in principle be more satisfactorily treated from the standpoint of the distribution of water between the alcohol and benzene. With sufficiently accurate distribution data over a range of concentration and temperature, estimates could be made of the heat of transference of water from the alcohol to the benzene phase, which could be combined with values of the relative partial molar heat content of water in aqueous alcohol to give the required heats of solution. An attempt was made to do this for the water–ethanol–benzene system, using the distribution data of Tarassenkov and Poloshinzewa (*Ber.*, 1932, **65**, 184), and the results of Bose (*Z. physikal. Chem.*, 1907, **58**, 585) on the heats of mixing of water and ethanol to give the partial molar heat contents. As the distribution data are not really comprehensive enough for the purpose, the presentation here of the modified figures obtained in this way does not seem justified. It may, however, be remarked that they do not differ by more than a few hundred calories from the ΔH values of Table II, and that they still rise slightly before falling rapidly to a fairly steady value. It therefore seems not unlikely that the variation with alcohol concentration of the true molar heat of solution of water in alcohol–benzene mixtures is much the same for methanol, ethanol, and butanol. But since there is less ambiguity in the ΔH values for solutions of butanol and the higher alcohols, the rest of the discussion will be confined to these systems, for which the variation of ΔH with alcohol concentration is shown graphically in Fig. 3.

Perhaps the most interesting feature of the experimental results is that for the butanol solutions ΔH first increases slightly as the alcohol concentration rises from zero, and does not start to fall rapidly until the mole-fraction of the alcohol is ~0·02. For octanol and pentanol, ΔH decreases from the start. As the monomer of the alcohol is in equilibrium with alcohol polymers, the heat absorbed, ΔH, when one mole of water dissolves in an infinite amount of a water–alcohol–benzene mixture is a composite quantity, made up of the heat absorbed by that part of the water which dissolves as such, the heat effect due to the association of the remainder with alcohol molecules, and the heat effect consequent on the shift in the alcohol monomer–polymer equilibrium. At the relatively low alcohol concentrations under consideration, we may regard the association of the alcohol molecules as limited to the formation of the lowest polymer. From spectroscopic studies (Kreuzer and Mecke, *Z. physikal. Chem.*, 1941, *B*, **49**, 309; Hoffmann, *ibid.*, 1943, *B*, **53**, 179) this appears to be the trimer and not the dimer. For any values of the heats of association and of the equilibrium constant for the trimerisation of the alcohol which in the light of the spectroscopic work seem at all reasonable, calculation shows that ΔH decreases continuously as the alcohol concentration rises from zero. Presumably, therefore, other factors are responsible for the maximum in ΔH at low alcohol concentrations in the butanol–benzene mixtures. We consider that one, at least, of these may be the dipole–induced dipole interaction between the polar alcohol molecules and the polarisable benzene molecules. Wolf (*Trans. Faraday Soc.*, 1937, **33**, 179) found that the molar heat of solution of ethanol in benzene (for the production of a very dilute solution) is about 2000 cals. less than the corresponding figure for hexane and *cyclo*hexane. This suggests that in an alcohol–benzene mixture, each alcohol molecule is in rather close association with one or more solvent molecules, and it may be that this solvation of the alcohol molecules produces a salting-out effect in that the quantity of benzene unaffected by the presence of the alcohol and capable of dissolving water in the normal way is appreciably less than the total amount of benzene present. If this is so, it means that the activity coefficient of the water is altered by the presence of the alcohol, and that the application of the law of mass action in its ideal form even to the dilute solutions we have considered is not strictly valid. It may also be remarked that the solubility of water in benzene is appreciably higher than that in other non-polar solvents, and that the heat of solution of water in benzene is ~1500 cals. less than that in petroleum, as assessed from Groschuff's solubility figures (*Z. Elektrochem.*, 1911, **17**, 348). These facts can likewise be attributed to dipole–induced dipole interaction between the water and benzene molecules. When water dissolves in the alcohol–benzene mixture it enters a medium in which some of the benzene molecules are already polarised by the alcohol, and it is possible that the dipole–induced dipole interaction energy between the water and benzene is reduced, so that effectively the heat of solution of that part of the water which dissolves as such is increased.

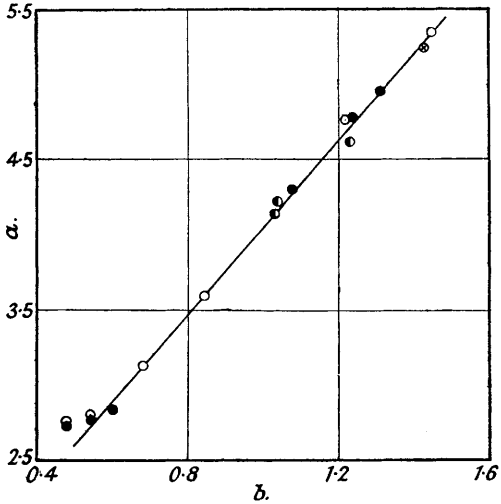
We may therefore, in general terms, tentatively attribute the peculiar course of the ΔH curve at low butanol concentrations to some sort of interaction between the hydroxyl group and the benzene which in turn affects the relationship between the benzene and the water. The simplest explanation of the fact that this abnormality in the trend of ΔH is less marked for benzene solutions of octanol and pentanol is that in these the hydroxyl group is in some way prevented from interacting so strongly with the neighbouring hydrocarbon molecules. This state of affairs would prevail if these alcohol molecules have a coiled configuration, so that the hydroxyl radical is to some extent screened by the alkyl group. It is possible that when flexible alcohol molecules are present in a solution at relatively low concentrations, they may tend to adapt themselves to conform to the geometry of the solvent molecules, so that stronger intermolecular attraction of the London kind and more economical molecular packing may be achieved. Girard and Abadie (*Discuss. Faraday Soc.*, 1946, **42**, *A*, 40) have in fact concluded from dispersion studies on octanol that in solution this molecule has the shape of an ellipsoid with three axes, whereas in the pure alcohol its shape is that of an ellipsoid of revolution.

The pentanol molecule, having five carbon atoms and one oxygen atom in a chain, could conceivably coil into a quasi-six-membered ring, the better to pack into the environment of hexagonal benzene molecules, and as a result the hydroxyl group would to some extent be screened, though not so completely as in coiled alcohol molecules with longer hydrocarbon chains. On this explanation, it would be expected that the differences observed in the ΔH curves for different alcohols in benzene would not necessarily arise with non-polar solvents the molecules of which are not cyclic. Thus, if a normal paraffin were used instead of benzene, higher alcohol molecules in solution in the paraffin might be encouraged to retain an open rather than a coiled configuration.

To test this conclusion, numerous attempts were made to measure the solubility of water in solutions of alcohols in hexane and in carbon tetrachloride, using the technique employed for the benzene experiments. Nothing conclusive resulted from these experiments, however. They are made much more difficult with these two solvents by the much lower solubility of the water, since on cooling a sealed tube containing water, alcohol, and the non-polar solvent, the opalescence accompanying the separation of the aqueous phase is very much fainter. Moreover, the irreproducibility of the values obtained with any one tube for the temperature at which the aqueous phase appeared could only be ascribed to variable supercooling effects. This was in marked contrast to the experiments with benzene, where the degree of reproducibility was very high, and where there was no reason to suppose that supercooling occurred to any significant extent.

FIG. 4.

Showing the linear relation between the quantities a *and* b *in the equation* $\log_{10} N = a - 10^3 b/T$ *for the solubility of water in mixtures of benzene and butanol (open circles), pentanol (full circles), and octanol (half-shaded circles). The circle with the cross is the point for pure benzene.*



As already explained, the variation with temperature of the solubility of water in any one alcohol–benzene solution obeys the relation $\log_{10} N = a - 10^3 b/T$. The factor b is, of course, proportional to the heat of solution, while the factor a is proportional to the entropy increase when a mole of water dissolves to give an arbitrary standard solution. In Fig. 4 values of a are plotted against b for all the mixtures of benzene with butanol, pentanol, and octanol which have been studied. The points conform to a straight line, except for those corresponding to the solutions of highest alcohol concentrations. In other words, at lower alcohol concentrations (but covering the range in which ΔH changes rapidly), there is a linear relation between the heat and entropy of solution of water. Other examples of this kind are known for binary solutions (see, *e.g.*, Butler, *Faraday Soc. Disc.*, Structure and Molecular Forces in Pure Liquids and Solutions, 1936, p. 229), but as yet they do not appear to have been given a satisfactory explanation.

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