173. *The Free Energy of the Normal Aliphatic Alcohols in Aqueous Solution. Part I. The Partial Vapour Pressures of Aqueous Solutions of Methyl,* n-*Propyl, and* n-*Butyl Alcohols. Part II. The Solubilities of Some Normal Aliphatic Alcohols in Water. Part III. The Theory of Binary Solutions, and its Application to Aqueous-Alcoholic Solutions.*

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PART I.

IT has been observed by one of us (Butler, *Proc. Roy. Soc.*, *A*, 1932, **135**, 366), judging by the somewhat fragmentary data available, that the difference between the molar free energy of the pure aliphatic alcohols and their standard free energy in dilute aqueous solution increases by an approximately constant amount for each additional CH_2 group. The partial pressures of ethyl-alcoholic solutions at 25° have been determined recently by Dobson (J., 1925, **127**, 2871) and by Shaw and Butler (*Proc. Roy. Soc.*, *A*, 1930, **129**, 519). The only extensive measurements of solutions of other alcohols are those of Vrewski (*Z. physikal. Chem.*, 1912, **81**, 1) on methyl and propyl alcohols at various temperatures above 30°, and of Ferguson and Funnel on methyl alcohol at 30° (*J. Physical Chem.*, 1929, **33**, 1). In order to complete the series, we have made determinations on solutions of methyl, *n*-propyl, and *n*-butyl alcohols over the accessible range of composition. For the higher alcohols the desired information can be obtained from a determination of the solubility in water, as shown in Part II, which contains the necessary data for the normal alcohols from C_5 to C_8.

Consider a binary mixture of water and an alcohol. Let N_1, N_2 be the respective molar fractions, and $\bar{F}_1$, $\bar{F}_2$ their partial molar free energies. If p_1, p_2 are their partial pressures over the solution and p_1^0, p_2^0 their vapour pressures as pure liquids at the same temperature, assuming that the vapours can be regarded as perfect gases, we have

$$\bar{F}_1 = F_1^0 + RT \log p_1/p_1^0;\ \bar{F}_2 = F_2^0 + RT \log p_2/p_2^0 \quad . \quad . \quad . \quad . \quad (1)$$

where F_1^0, F_2^0 are the molar free energies of the pure liquids. In a solution which obeys Raoult's law, the partial vapour pressure of each component is proportional to its molar fraction, *i.e.*, $p_1/p_1^0 = N_1$, $p_2/p_2^0 = N_2$. When Raoult's law is not obeyed we may write

$$p_1/p_1^0 = N_1 f_1;\ p_2/p_2^0 = N_2 f_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where f_1, f_2 are the activity coefficients, which, as defined in this way, are obviously equal to unity in the pure liquid. Introducing these values of p_1/p_1^0, p_2/p_2^0 into (1), we have

$$\bar{F}_1 = F_1^0 + RT \log N_1 f_1;\ \bar{F}_2 = F_2^0 + RT \log N_2 f_2 \quad . \quad . \quad . \quad . \quad (3)$$

On the other hand, in a very dilute solution of the alcohol, its partial free energy is necessarily related to the concentration by a relation which, if it be assumed that at infinite dilution the alcohol molecules are not appreciably associated, may be written in the form

$$\bar{F}_2 = (\bar{F}_2^0)_W + RT \log N_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $(\bar{F}_2^0)_W$ is the standard molar free energy for the dilute aqueous solution. If f_2^0 is the activity coefficient in this dilute solution, according to (3) it is evident that

$$(\bar{F}_2^0)_W - F_2^0 = RT \log f_2^0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

f_2^0 may be determined by extrapolating the values of the activity coefficient determined in fairly dilute solutions to zero concentration. The quantity $RT \log f_2^0$ obtained in this way measures the difference between the molar free energy of the pure alcohol and its standard free energy in very dilute aqueous solutions. This difference can be regarded as a measure of the free energy effect of removing from a given alcohol molecule all the surrounding alcohol molecules and replacing them by water.

Similarly if f_1^0 is the activity coefficient of water in any solvent, referred to pure water as unity, at infinite dilution, and $(\bar{F}_1^0)_A$ is the standard free energy defined as above in this solvent,

$$(\bar{F}_1^0)_A - F_1^0 = RT \log f_1^0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

EXPERIMENTAL.

Materials.—Methyl alcohol. Acetone (about 0·1%) was removed by adding excess of I and NaOH aq. and refluxing it until there was no further smell of CHI_3; some H_2O was added, and the MeOH fractionated, that boiling within 1° of the correct value being collected. It was finally dried with Al–Hg (Hartley and Raikes, J., 1925, **127**, 524); b. p. (corr.) 64·46°, $D_{4°}^{25°}$ 0·78643.

n-*Propyl alcohol.* The main impurities in the commercial alcohol were allyl alcohol and H_2O. The amount of the former was estimated by titration with KBr–$KBrO_3$ aq. A small excess of Br was added, and after standing over-night, the alcohol was fractionated, that distilling at 95—98° being collected. This was kept over CaO for a week and then refluxed and fractionated. The middle fraction was collected at 97·19° ± 0·02°/760 mm.; $D_{4°}^{25°}$ 0·7999.

n-*Butyl alcohol.* This was dried over CaO for a week, refluxed for 8 hr., and fractionated; the whole distilled between 118·19° and 118·35° at 775·3 mm. The middle fraction [b. p. 117·71° (corr.)] was collected; $D_{4°}^{25°}$ 0·8055.

Method.—The apparatus has already been described (Shaw and Butler, *loc. cit.*). In principle the method is as follows. A measured vol. of dry, CO_2-free air is bubbled through the solution, and the satd. vapour is condensed in a tube immersed in a bath of solid CO_2 and Et_2O. In these determinations it was convenient to make two separate expts. on each solution: (1) the wt. of condensed vapour carried by a known vol. of air was determined; (2) a larger unmeasured vol. of air was passed, and the compn. of the condensate determined by one or other of the following methods according to circumstances. (i) With most of the PrOH solutions, the condensate was compared directly with solutions of known compn. in the Zeiss industrial interferometer, a rough comparison being made first in order to fix the approx. compn. Two solutions were then prepared accurately, one containing a slightly greater and the other a slightly smaller proportion of PrOH than the unknown, the compn. of which was then determined by assuming a linear relationship between interferometer reading and compn. The refractive index curve of these solutions has a max., in the vicinity of which the interferometer is insensitive. These solutions were diluted with a weighed amount of H_2O, so as to bring the compn. into a more favourable region.

(ii) The BuOH condensates in some cases had two phases, and these were diluted with sufficient H_2Q to produce a homogeneous solution.

(iii) The MeOH condensates could not be measured without dilution on account of evaporation from the interferometer cell during the readings; they were therefore diluted with H_2O to a concn. not exceeding 8%. The loss of accuracy consequent on the dilution was partly compensated by using a long (5 cm.) cell in the interferometer. It is extremely difficult with these dil. solutions to identify similar fringes, and a mistake of a single fringe causes a considerable error. In these cases, a comparison was made between the unknown and the calibration solutions with three cells of different thicknesses (0·5, 1·0, and 5·0 cm. approx.). The compn. corresponding to the various possible fringe readings was worked out for the three cells, and the proper fringes were identified by the criterion that the determined compn. must be the same for all the cells, which is the case for one choice of fringes but for no other.

The partial pressures were calculated in the following way. If a vol. V of dry air is satd. by the solution at the temp. t and at atm. press. P, and the condensate contains w_1 g. of H_2O and w_2 g. of alcohol, the vols. of H_2O and alcohol (mol. wts. M_1 and M_2) respectively in the vapour are given (in c.c.) by

$$v_1 = w_1 \times 22{,}400 \times (273 + t) \times 760/(M_1 \times 273 \times P),$$
$$v_2 = w_2 \times 22{,}400 \times (273 + t) \times 760/(M_2 \times 273 \times P).$$

The total vol. of the satd. air is thus $V + v_1 + v_2$, and the partial pressures are

$$p_1 = Pv_1/(v_1 + v_2 + V);\quad p_2 = Pv_2/(v_1 + v_2 + V).$$

TABLE I.

Partial pressures of water–alcohol solutions at 25°.

Methyl alcohol solutions ($n = 1$).

N_2.	P.	w.	x.	p_2.	p_1.	N_2.	P.	w.	x.	p_2.	p_1.
0·0202	755 759	0·0477 0·0476	23·0	3·85	22·9	0·2017	760 757	0·1386 0·1389	76·6	35·8	19·5
0·0403	759 758·5	0·0577 0·0579	38·0	7·67	22·3	0·3973	750 746·5	0·2093 0·2095	87·0	59·6	15·8
0·0620	763 759	0·0699 0·0696	48·5	11·7$_6$	22·2	0·6579	742·5 751	0·2894 0·2891	93·5	85·7	10·5
0·0791	755·5 752	0·0780 0·0780	55·8	15·1	21·2	0·8137	742·0 759	0·3469 0·4179	97·2	104·6	5·26
0·1145	749 739	0·0973 0·0974	64·4	21·5	21·1	1·000	750 740	0·4198 0·4197	100·0	126·6	0·0

Propyl alcohol solutions ($n = 2$, except in first four detmns., where $n = 3$).

N_2.	P.	w.	x.	p_2.	p_1.	N_2.	P.	w.	x.	p_2.	p_1.
0·0100	740 735	0·0752 0·0753	27·6	2·68	23·4	0·6000	756 762	0·1127 0·1126	72·1	15·5	19·9
0·0200	765 761	0·0943 0·0943	41·7	5·05	23·5	0·8000	747 750	0·1138 0·1138	81·6	17·8	13·4
0·0500	770 773	0·0930 0·0925	60·8	10·8	23·2	0·9000	759 764	0·1131 0·1131	88·8	19·4	8·13
0·1000	757 766	0·1048 0·1048	65·9	13·2	22·7	0·9500	771 766	0·1141 0·1141	94·3	20·8	4·20
0·2000	777 775	0·1054 0·1054	67·4	13·6	21·8	1·000	770 774	0·1120 0·1119	100·0	21·76	0·0
0·4000	744 751	0·1085 0·1086	68·5	14·2	21·7						

Butyl alcohol solutions ($n = 3$ except where otherwise noted).

N_2.	P.	w.	x.	p_2.	p_1.	N_2.	P.	w.	x.	p_2.	p_1.
* 0·0100	756 754	0·1108 0·1108	34·3	2·97	23·4	0·850	765 767	0·0873 0·0873	65·0	5·98	13·2
0·0188 and 0·4876	756 756	0·1008 0·1008	46·5	4·87	23·0	† 1·000	756 755	0·1082 0·1082	100·0	6·96	0·0
0·700	756 756	0·0986 0·0988	52·2	5·37	20·2						

* $n = 4$. † $n = 5$.

Results.

In Table I, N_2 is the mol. fraction of the alcohol, n the number of measured vols. of air passed through the solution (each vol. being 773·7 c.c. at 25°), P the mean atm. press. during the expt., and w the wt. of the condensate (at least two determinations of this wt. were made with each solution). A few determinations which showed a considerable divergence from the others have been rejected. x is the mean wt. % of alcohol in the condensate, as determined in separate expts., and p_1, p_2 the mean partial pressures of H_2O and the alcohol. Table II gives the activity coeffs. $f_1 = p_1/p_1^0N_1$, $f_2 = p_2/p_2^0N_2$. The v. p. of H_2O at 25° has been taken as 23·77 mm.

FIG. 1.

Partial vapour-pressure ratios of the alcohols in aqueous solutions. △ = *Dobson; all other points by Shaw and Butler, or from this paper.*

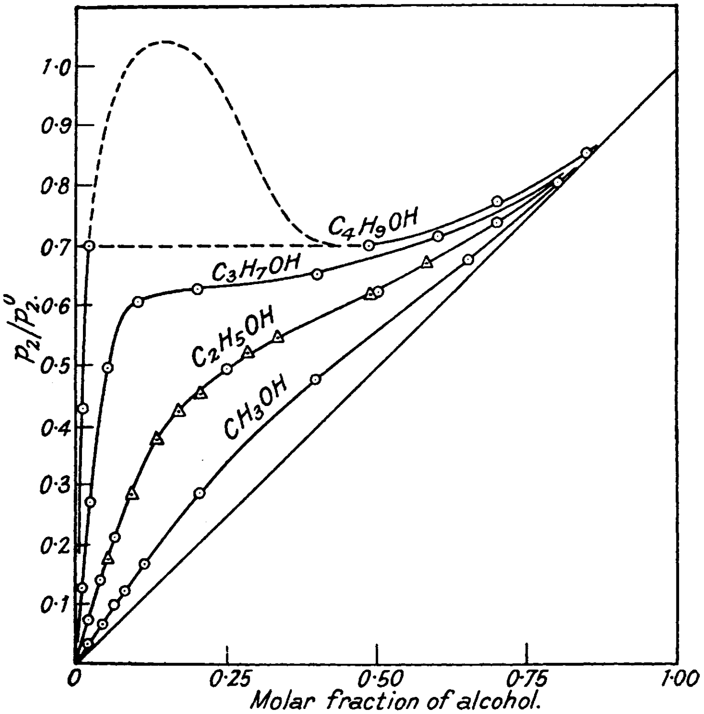


TABLE II.

Activity coefficients in water–alcohol solutions.

Methyl alcohol.			n-Propyl alcohol.			n-Butyl alcohol.		
N_2.	f_2.	f_1.	N_2.	f_2.	f_1.	N_2.	f_2.	f_1.
0·000	—	1·00	0·00	—	1·00	0·00	—	1·00
0·0202	1·505	0·98	0·01	12·3	0·99	0·01	42·7	1·00
0·0403	1·503	0·98	0·02	11·6	1·01	0·019*	37·2	0·99
0·0620	1·498	1·00	0·05	9·92	1·03	0·488*	1·44	1·89
0·0791	1·505	1·02	0·10	6·05	1·06	0·70	1·10	2·83
0·1145	1·482	1·01	0·20	3·12	1·15	0·85	1·01	3·70
0·2017	1·403	1·03	0·40	1·63	1·52	1·00	1·00	—
0·3973	1·186	1·10	0·60	1·19	2·10			
0·6579	1·029	1·30	0·80	1·02	2·82			
0·8137	1·008	1·42	0·90	0·99	3·42			
1·000	1·00	—	0·95	1·01	3·54			
			1·00	1·00	—			

* Limits of miscibility.

DISCUSSION.

The vapour-pressure ratios (p_2/p_2^0) of the alcohols in the solutions are shown in Fig. 1. The rapidly increasing deviation from Raoult's law, which is represented by the straight line, as we pass up the series, is conspicuously exhibited. Figs. 2 and 3 show respectively the activity coefficients of the alcohols (logarithmic) and of water in the various solutions. Although there is an inaccessible region of incomplete miscibility in the butyl-alcoholic solutions, the activity coefficients are compatible with a continuous curve of the same type as the others; approximate values in the inaccessible region have been obtained by completing the curve (see Fig. 2), and the partial vapour pressures of the unstable solutions, shown by the broken line in Fig. 1, were obtained by the use of activity coefficients thus estimated.

FIG. 2.

Activity coefficients of lower normal alcohols in aqueous solutions.

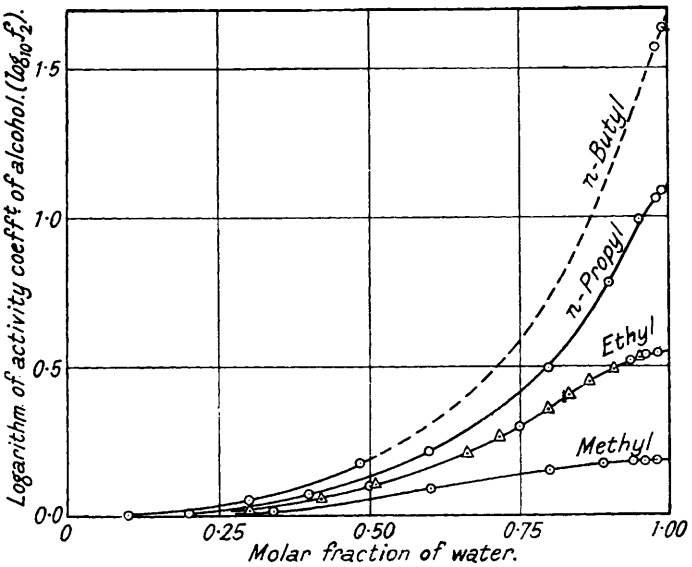
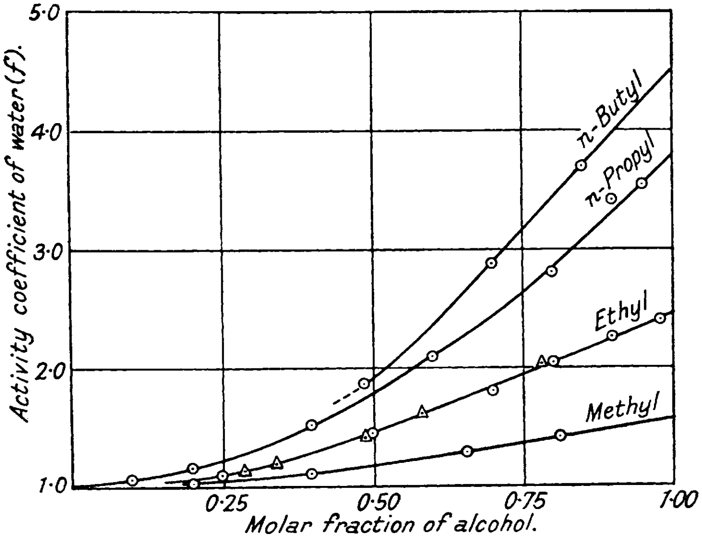


FIG. 3.

Activity coefficients of water in alcoholic solutions.



The deviation from Raoult's law shown by propyl alcohol is only slightly less than that which would cause separation into two layers. That the addition of a salt causes separation into two layers is a consequence of the fact, demonstrated by Shaw and Butler (*loc. cit.*), that the salt increases the partial pressure of the alcohol in its more dilute solutions and decreases its partial pressure in more concentrated solutions. In the presence of a moderate constant concentration of a salt, the partial-pressure curve of propyl alcohol will thus have a maximum, and in consequence separation into two layers will take place.

TABLE III.

Activity coefficients and standard free energies of alcohols in water, and of water in alcohols, at infinite dilution.

Alcohol.	Methyl.	Ethyl.	*n*-Propyl.	*n*-Butyl.
f_2^0	1·507	3·48	12·5	46·5
$(\bar{F}_2^0)_W - F_2^0$, cals.	243	740	1500	2280
f_1^0	1·62	2·52	3·80	4·68
$(\bar{F}_1^0)_A - F_1^0$, cals.	290	550	790	910

The values of the activity coefficients of alcohols and water at infinite dilution, obtained by extrapolation from the measured values, are given in Table III, together with values of $(\bar{F}_2^0)_W - F_2^0$ and $(\bar{F}_1^0)_A - F_1^0$. The extrapolation for water was made with the help of a linear relation obtained later (p. 685). The general significance of these results is discussed in Part III (p. 682).

PART II.

WHEN the alcohol and water are incompletely miscible, the activity of the alcohol must be the same in the two phases which are in equilibrium with each other; hence $f_2N_2 = f_2'N_2'$, where N_2, N_2' are the molar fractions in the aqueous and the alcoholic layer. We thus have for the activity coefficient of alcohol in the aqueous phase $f_2 = f_2'N_2'/N_2$. If the alcohol-rich phase contains only a small proportion of water, the activity of the alcohol can be taken as unity, so that $f_2 = 1/N_2$. If the aqueous phase is also dilute, this value can be taken as equal to f_2^0. The errors made in these approximations compensate each other to some extent; *e.g.*, although the molar fraction of butyl alcohol in the alcohol-rich phase is only 49%, the value of f_2^0 determined by the vapour-pressure measurements is 46·5, while $1/N_2 = 53·1$. With the higher alcohols the difference would be less and the values of $(\bar{F}_2^0)_W - F_2^0$ are given with sufficient accuracy for our purpose by

$$(\bar{F}_2^0)_W - F_2^0 = RT \log f_2^0 = -RT \log N_2.$$

EXPERIMENTAL.

Materials.—All the alcohols were purchased (B.D.H.), and purified as follows. *n*-Amyl alcohol was repeatedly fractionated under a 30-cm. Hempel column in an all-glass apparatus. The middle fraction was finally dried with Ca and fractionated; b.p. 137·60—137·70° (corr.), $D_{4^\circ}^{25^\circ}$ 0·81146; $n_D^{20^\circ}$ 1·41043.

n-Hexyl alcohol was fractionated several times in vac. with a Hempel column, and the middle fractions refluxed with Ca and refractionated; b. p. 80·8—80·9°/12 mm., 155·7°/760 mm.; $D_{4^\circ}^{25^\circ}$ 0·81648; $n_D^{20^\circ}$ 1·41778.

n-Heptyl alcohol was similarly purified; b. p. 87·5—87·6°/9 mm., 175·6°/760 mm.; $D_{4^\circ}^{25^\circ}$ 0·81960; $n_D^{20^\circ}$ 1·42337.

n-Octyl alcohol was similarly purified; b. p. 94·80—94·85°/8 mm., 194·5°/760 mm.; $D_{4^\circ}^{25^\circ}$ 0·82238; $n_D^{20^\circ}$ 1·42937.

The Mutual Solubility of n-*Butyl Alcohol and Water at* 25°.—The mutual solubilities of BuOH and H_2O have been determined by Hill and Malisoff (*J. Amer. Chem. Soc.*, 1926, **48**, 918), using a volumetric method. To check these with our sample of the alcohol, Sidgwick's method (J., 1911, **99**, 1122) was adopted. Solutions of suitable compn., prepared by weighing, were placed in a soda-glass flask fitted with a thermometer. In the case of the water-rich solutions, the flask was constantly shaken in a large beaker of H_2O which was slowly heated, and the temp. at which the first signs of cloudiness appeared was noted. The temp. at which cloudiness disappeared, which was more easily recognised, was also observed. Successive readings did not differ by more than 0·05°. Similar observations were made, in the reverse order, with alcohol-rich phases. These determinations were repeated in Pyrex-glass flasks, but no difference was found in the results, although Mueller, Pugsley, and Ferguson (*J. Physical Chem.*, 1931, **35**, 1314) found a consolute temp. 0·4° lower in this glass.

TABLE I.

Mutual solubilities of butyl alcohol and water.

Butyl alcohol, % by wt.	7·497	7·407	7·318	7·202	7·090	7·016	79·28	79·50	79·73	80·01
Temp. (±0·03°)	22·60°	23·70°	24·85°	26·40°	28·06°	29·18°	30·83°	27·45°	23·40°	18·45°

Composition of saturated layers at 25°: Aqueous phase, 7·31% (wt.) or 1·882 mols. %; alcoholic phase, 79·64% (wt.) or 48·76 mols. %. These are in good agreement with the determinations of Hill and Malisoff, *viz.*, 7·35% and 79·73% by wt., respectively.

Solubility Determination of the Higher Alcohols.—An analytical method was employed. The apparatus was a U-tube arrangement having two internal stoppers. Suitable quantities of the alcohol and H_2O were placed in one of the connected vessels, and shaken in the thermostat at 25° for some hr. The liquid was then allowed to separate into two layers, and the heavier aq. layer was separated by raising the stoppers and allowing part of the liquid to run into the connected vessel. A weighed portion of the separated solution was diluted with about an equal quantity of H_2O, and the resulting solution compared with calibration solutions of known compn. in the interferometer. To avoid the possibility of reading the position of the wrong fringe, two cells (1 cm. and 5 cm.) were used (see p. 676). The results of the determinations are given in Table II.

TABLE II.

Solubilities of higher aliphatic alcohols in water.

n-Amyl alcohol. Wt. % : 2·209, 2·203, 2·207, 2·212, 2·211; mean 2·208. $N_2 = 0{\cdot}00459_6$.
n-Hexyl alcohol. Wt. % : 0·637, 0·625, 0·622, 0·615, 0·611, 0·627, 0·634; mean 0·624. $N_2 = 0{\cdot}00110_7$.
n-Heptyl alcohol. Wt. % : 0·179, 0·184, 0·180, 0·182, 0·180, 0·179, 0·182; mean $0{\cdot}180_7$. $N_2 = 0{\cdot}000280_8$.
n-Octyl alcohol. Wt. % : 0·0571, 0·0606, 0·0590, 0·0587, 0·0582, 0·0580; mean 0·0586. $N_2 = 0{\cdot}0000811$.

No suitable method for determining the compn. of the alcohol-rich layers has yet been found. The above method failed because the alc. phases tended to creep up the sides of the interferometer cell and no stoppered cell was available; insufficient accuracy was obtained by adding sufficient H_2O to dissolve the alc. phase, and the variation of viscosity with compn. for small additions of H_2O to the higher alcohols was too small. An approx. determination of the solubility of H_2O in n-$C_5H_{11}{\cdot}OH$ at 25° gave $N_2' = 0{\cdot}71$.

Table III gives the values of f_2^0 and $(\bar{F}_2^0)_W - F_2^0$ for the whole series of alcohols, Δ being the differences of the latter between successive members of the series. Except for the first two alcohols, the difference is approx. const. and its mean value is 806 cals.,* *i.e.*, each CH_2 group after the second contributes about 800 cals. to the difference of the free energy of the molecule in the pure alcohol and in water.

TABLE III.

Activity coefficients and standard free energies of aliphatic alcohols in dilute aqueous solution.

Alcohol.	f_2^0.	$(\bar{F}_2^0)_W - F_2$.	Δ.	Alcohol.	f_2^0.	$(\bar{F}_2^0)_W - F_2$.	Δ.
Methyl	1·51	240	—	*n*-Amyl *	219	3190	910
Ethyl	3·48	740	500	*n*-Hexyl *	903	4030	840
n-Propyl	12·5	1500	760	*n*-Heptyl *	3,560	4850	820
n-Butyl	46·5	2280	780	*n*-Octyl *	12,300	5580	730

* In these cases f_2^0 is taken as $1/N_2$.

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* The value of $(\bar{F}_2^0)_W - F_2^0$ for amyl alcohol is probably somewhat high, because the inaccuracy of the solubility method is greatest with this substance, but it is probable that the gradual decrease of Δ shown by the higher members of the series is real.

PART III.

WE shall attempt to account for the main features of the behaviour of water-alcohol solutions in terms of the cohesive or adhesive forces between the molecules. It is difficult to discuss the effects of intermolecular forces in a liquid except in terms of the surfaces of contact of the molecules. It has long been known that there is a close parallelism between the mutual solubility of liquids and their interfacial energy. However, owing to the orientation of molecules at macroscopic interfaces, the observed interfacial energy cannot be taken as a measure of the forces operating over the whole surface of the molecules in solution. Harkins, Brown, and Davies (*J. Amer. Chem. Soc.*, 1917, **39**, 354), while pointing out the general connexion between solubility and interfacial energy, realised this, and remarked that " true solubility is a molecular scale phenomenon and is dependent upon the attractions of the different parts of various molecules on each other, and upon the shapes and sizes of the molecules which must be fitted together to make a solution." Langmuir (*Coll. Symp. Monographs*, 1925, **3**, 48) has given greater precision to this conception by his " principle of independent surface action," which postulates that the intermolecular energy in a liquid can be obtained by summing the interfacial energies of the various surfaces of contact. On the assumption that the molecules are distributed and orientated entirely at random, he obtained for a binary solution of two substances A and B the equations $\log f_A = \beta^2 S_A \phi$, $\log f_B = \alpha^2 S_B \phi$, where S_A, S_B are the surface areas of molecules of A and B; α and β are their surface fractions in the solution; and ϕ is the " mixture energy." If the molecule A has two kinds of surface, A and C, the fractional areas of which are a and c, and the molecule B two kinds of surface, B and D, having the fractional areas b and d, $\phi = ab\gamma_{ab} + ad\gamma_{ad} + bc\gamma_{bc} + cd\gamma_{cd} - ac\gamma_{ac} - bd\gamma_{bd}$, where γ_{ab} is the interfacial energy for the surface between A and B, etc. Smyth and Engel (*J. Amer. Chem. Soc.*, 1929, **51**, 2646, 2660) determined the partial pressures of a number of binary solutions, chosen so as to test these equations, and found that while they showed a general qualitative agreement, quantitatively there were considerable deviations which they attributed to the influence of the electric dipoles present in the molecules.

The discussion given below is based on Langmuir's theory, but the " mixture energy " is evaluated in a different way. In particular, instead of using the " surface energy " of molecules in the vapour state, we have introduced terms representing the cohesive or adhesive work between two like or unlike surfaces. As a result of this modification, which brings out certain relations which are not clearly apparent in Langmuir's form of the theory, the expression for the " mixture energy " takes a different form, but the equations are not otherwise altered.

Work of Transfer of a Molecule from its Pure Liquid to Another Solvent.—Consider first a substance A of which all parts may be considered alike. We shall calculate the energy required to remove a molecule from the pure liquid into a very dilute solution in an (also homogeneous) solvent B. Let the area of the molecule be S_A. In order to remove A from its liquid we must do work on account of the cohesive forces between it and surrounding molecules, which we can write $S_A\gamma_{AA}$. This leaves a cavity of area S_A in the liquid, in the collapse of which we obtain the work $S_A\gamma_A$, where $\gamma_A = \gamma_{AA}/2$ may be regarded as the surface tension. The total work required is thus $S_A\gamma_A$. In order to bring the molecule into the solvent B, we must first make a cavity in this solvent having area S_A (work required $S_A\gamma_B$). On introducing the molecule A, we obtain the work of adhesion between A and the surrounding B molecules, *viz.*, $S_A\gamma_{AB}$. The total work required to effect the transfer is thus

$$S_A\phi_{A(B)} = S_A(\gamma_A + \gamma_B - \gamma_{AB}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and we may write $kT \log f^0_{A(B)} = S_A\phi_{A(B)}$.

Hildebrand (" Solubility," 1924) has elaborated a theory of solubility in which deviations from Raoult's law in non-polar solutions are regarded as mainly due to differences of the internal pressures of the two liquids. On this theory, two liquids having equal internal pressures may be expected to give ideal solutions, and in other cases the deviation from ideality is approximately proportional to the internal-pressure difference of the two pure liquids. The internal pressure of a liquid is a measure of the cohesion between the molecules, and in the absence of polarity is approximately proportional to the surface tension. On Hildebrand's theory the deviation from Raoult's law is thus approximately determined by $\gamma_A - \gamma_B$. It is known, however (cf. Adam, " Chemistry and Physics of Surfaces," p. 148), that at macroscopic interfaces the work of adhesion of two surfaces is often approximately equal to the smaller work of cohesion, *i.e.*, $2\gamma_B = \gamma_{AB}$. In such a case (1) reduces to $\phi = S_A(\gamma_A - \gamma_B)$, which is equivalent to Hildebrand's theory.*

If the molecules A and B have not homogeneous surfaces, the work of transfer of A from the pure liquid to a dilute solution in the solvent B is still given by $S_A\phi_{A(B)} = S_A(\gamma_A + \gamma_B - \gamma_{AB})$, where $S_A\gamma_A$ is the work required to remove the molecule A from its own liquid, $S_A\gamma_B$ is the work required to make a cavity of area S_A in B, and $S_A\gamma_{AB}$ the work of adhesion between the molecule A and surrounding molecules of B, but these quantities are themselves complex.

We will consider the evaluation of these terms in a simple case. Suppose that the surface of the molecule A is of two kinds, P and Q, having areas S_P and S_Q. Let $p = S_P/S_A$, $q = S_Q/S_A$, be the fractions of the surface occupied by P and Q. Suppose that the surface of B is homogeneous. Consider a molecule A in its own liquid. If the molecules are distributed entirely at random, of the area S_P a fraction p will be in contact with a P surface and a fraction q with a Q surface; and of the area S_Q, fractions p and q will be in contact with P and Q surfaces respectively. The areas of the PP, QQ, and PQ interfaces of a molecule will thus be p^2S_A, q^2S_A, $2pqS_A$. In order to remove a molecule from the liquid, leaving a cavity of area S_A, the work required is thus $S_A(p^2\gamma_{PP} + q^2\gamma_{QQ} + 2pq\gamma_{PQ})$, where γ_{PP}, γ_{QQ} are the work of cohesion between P and P, or Q and Q, and γ_{PQ} is the work of adhesion between P and Q. The work obtained in the collapse of the cavity is easily shown to be half this quantity, so that the work of removing the molecule may be written $S_A(p^2\gamma_P + q^2\gamma_Q + pq\gamma_{PQ})$, and we have $\gamma_A = p^2\gamma_P + q^2\gamma_Q + pq\gamma_{PQ}$. The work of removing the molecule A from the solvent B, leaving a cavity of area S_A is similarly $S_A(p\gamma_{PB} + q\gamma_{QB})$, *i.e.*, $\gamma_{AB} = p\gamma_{PB} + q\gamma_{QB}$, and the work obtained in the collapse of the cavity is γ_B. In this case, therefore,

$$\phi_{A(B)} = p^2\gamma_P + q^2\gamma_Q + pq\gamma_{PQ} - p\gamma_{PB} - q\gamma_{QB} + \gamma_B \quad . \quad . \quad . \quad . \quad (2)$$

The work required to transfer a molecule of B from the liquid B to the solvent A may be written $S_B\phi_{B(A)}$, and it is easily shown that $\phi_{B(A)} = \phi_{A(B)}$. Writing both these quantities ϕ, we have

$$kT \log f^0_{A(B)} = S_A\phi; \quad kT \log f^0_{B(A)} = S_B\phi \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We have now to see how far these relations are applicable to the water–alcohol solutions. Let A be the alcohol molecule, P being the hydrocarbon chain and Q the hydroxyl group, and B the water molecule. As we pass up the series of alcohols, p, the fractional surface area of the hydrocarbon chain, gradually increases and approaches unity, while q approaches zero, and it is evident from (2) that ϕ approaches the limiting value

$$\phi_l = \gamma_P - \gamma_{PB} + \gamma_B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The activity coefficient of water in alcohol should therefore approach a constant value given by $kT \log f^0_{B(A)} = S_B\phi_l$ (since S_B is constant), while the activity coefficient of alcohol in water should approach the value $kT \log f^0_{A(B)} = S_A\phi_l$, where S_A increases by constant increments. In Table I it is shown that both these requirements are fulfilled. The ratio $\log f^0_{A(B)}/\log f^0_{B(A)}$ should also be equal to S_A/S_B. The table gives the values of S_A/S_B calculated in this way. This ratio increases by about 0·5 for each additional $-CH_2$ group, indicating that the increase of the surface caused by the latter is about half that of the water molecule. This is a reasonable figure, but the absolute magnitudes of S_A/S_B are less than might be expected from the molecular dimensions.

It may be observed, however, that constant increments in $\log f^0_{A(B)}$ are reached at an earlier point in the series than would be expected according to (2), *i.e.*, (2) approaches its

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* This expression is analogous to Antonow's equation for the interfacial energy between two liquids $\sigma_{AB} = \sigma_A - \sigma_B$. This is often approximately valid for the reason given.

TABLE I.

Alcohol.	$\log f^0_{B(A)}$.	$\log f^0_{A(B)}$.	S_A/S_B.	Alcohol.	$\log f^0_{B(A)}$.	$\log f^0_{A(B)}$.	S_A/S_B.
Methyl	0·21	0·18	0·9	Butyl	0·67	1·67	2·6
Ethyl	0·40	0·54	1·4	Amyl	0·72[*]	2·34	3·2
Propyl	0·58	1·11	1·9				

[*] Estimated from the solubility of water.

limiting value (4) too quickly. It must be remembered that it has been assumed that the molecules are distributed entirely at random. If the alcohol molecules are orientated in the pure liquid in such a way that the fraction of PP surfaces is greater than in a random distribution, (2) would be closer to its limiting value (4) than would correspond to the surface fractions p and q.

Work of Transfer of a Molecule from its Pure Liquid to a Binary Solution.—Let the number of molecules of A and B in a quantity of the solution be n_A, n_B. If S_A, S_B are the surface areas of the molecules, the surface fractions of surfaces A and B in the solution are $\alpha = n_AS_A/(n_AS_A + n_BS_B)$, $\beta = n_BS_B/(n_AS_A + n_BS_B)$. If the molecules are distributed entirely at random, of the total surface of the molecule A a fraction α is in contact with A surfaces, and a fraction β with B surfaces. The work required to remove the molecule A, leaving a cavity in the liquid, is $S_A(\alpha\gamma_{AA} + \beta\gamma_{AB})$. The work obtained in the collapse of the cavity is easily shown to be $\frac{1}{2}S_A(\alpha^2\gamma_{AA} + \alpha\beta\gamma_{AB} + \beta^2\gamma_{BB})$. Since $\alpha = 1 - \beta$, the difference between these quantities can be expressed as $S_A[\gamma_A - \beta^2(\gamma_A + \gamma_B - \gamma_{AB})]$ and the work of transfer from pure A to the solution is thus $S_A\beta^2(\gamma_A + \gamma_B - \gamma_{AB})$. The activity coefficient of A in the solution is therefore given by

$$kT \log f_{A(AB)} = S_A\beta^2\phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $\phi = \gamma_A + \gamma_B - \gamma_{AB}$, as before.[*]

Similarly by considering the transfer of B from its pure liquid to the solution, we obtain

$$kT \log f_{B(AB)} = S_B\beta^2\phi \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

These equations apply also when one or both of the molecules A, B have mixed surfaces, but in these cases γ_A, γ_B, γ_{AB} are composite quantities constructed as in the example given above. Thus, if the surface of A is occupied by a fraction p of P and q of Q, and the surface of B by a fraction r of R and t of T, we shall have: $\gamma_A = p^2\gamma_P + q^2\gamma_Q + pq\gamma_{PQ}$; $\gamma_B = r^2\gamma_R + t^2\gamma_T + rt\gamma_{RT}$; $\gamma_{AB} = pr\gamma_{PR} + pt\gamma_{PT} + qr\gamma_{QR} + qt\gamma_{QT}$.

Application to Water–alcohol Solutions.—Applying these relations to the water–alcohol solutions, we have $\log f_A = \beta^2S_A\phi/kT$, $\log f_B = \alpha^2S_B\phi/kT$, where α and β are the surface fractions of alcohol and water. In computing the values of α and β the following relative areas have been found to give the closest agreement with these equations: water 1, methyl alcohol 1·4, ethyl alcohol 1·8, propyl alcohol 2·2, butyl alcohol 2·6. Figs. 4 and 5 show $\log f_A$ and $\log f_B$ plotted against β^2 and α^2 respectively. It is evident that the equations hold extremely well between molar fractions 1·00 and 0·15 of the alcohol, but in more dilute solutions there is a marked deviation from the linear relation, the activity coefficients being less than is required by the equation. A similar deviation appears in the same region in the curves for water. The agreement between the observed activity coefficients of the alcohols, and the values calculated from $\log f_A = \beta^2\theta_A$, $\theta_A = S_A\phi/kT$ being obtained by extrapolating the linear parts of the curves to $\beta^2 = 1$, is shown in Table II.

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[*] It has been shown that the experimental value of the increment of $RT \log f^0_{A(B)}$ for each additional $-CH_2$ group is about 800 cal./g.-mol. It is of interest to see if this agrees with the value obtained from (4), using the macroscopic values of the surface free energies. The surface free energies of hydrocarbons and water at 25° are about 20 and 70 ergs/cm.^{2}, and the work of adhesion of hydrocarbon to water about 40 ergs/cm.^{2}. ϕ is thus about 50 ergs/cm.^{2}. If N^0 is the Avogadro number and ΔS_A the increase of area of the alcohol molecule for each additional $-CH_2$ group, which we estimate as 22 Å.^{2}, we have $\Delta(RT \log f_{A(B)}) = N^0 \, . \, \Delta S_A \, . \, \phi_l = 1600$ cals. This is about 100% too high, but since the surface energies of cavities and surfaces of molecular dimensions must differ considerably from the macroscopic values at plane surfaces, the agreement is probably as good as could be expected.

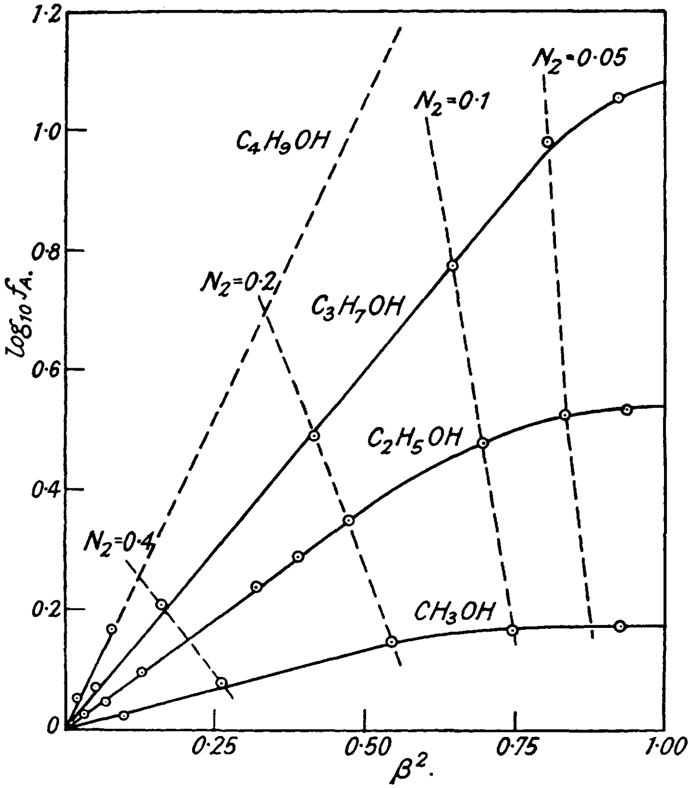
TABLE II.

Agreement of observed activity coefficients with $\log_{10} f_A = \beta^2\theta_A$.

	Methyl alcohol. $S_A/S_B = 1·4$; $\theta_A = 0·27$.			Ethyl alcohol. $S_A/S_B = 1·8$; $\theta_A = 0·74$.			Propyl alcohol. $S_A/S_B = 2·2$; $\theta_A = 1·20$.		
N_A.	β^2.	$\log f_A$ (calc.).	$\log f_A$ (obs.).	β^2.	$\log f_A$ (calc.).	$\log f_A$ (obs.).	β^2.	$\log f_A$ (calc.).	$\log f_A$ (obs.).
0·1	0·749	0·202	0·173	0·695	0·515	0·48	0·645	0·775	0·78
0·2	0·548	0·148	0·148	0·473	0·350	0·35	0·416	0·500	0·48
0·4	0·267	0·072	0·072	0·206	0·152	0·15	0·164	0·197	0·21
0·6	0·104	0·028	0·021	0·073	0·054	0·05	0·054	0·065	0·076
0·8	0·027	0·007	0·004	0·015	0·011	—	0·010	0·012	—

FIG. 4.

Logarithm of activity coefficients of alcohols plotted against β^2.



The values of θ_A, θ_B obtained from the linear parts of the curves differ somewhat from those given previously * from a consideration of the extremities only. Table III shows that their ratio is in fair agreement with the assumed values of S_A/S_B.

TABLE III.

	θ_A.	θ_B.	S_A/S_B (from slopes).	S_A/S_B (assumed).
Methyl	0·27	0·22	1·2	1·4
Ethyl	0·74	0·42	1·7	1·8
Propyl	1·20	0·60	2·0	2·2
Butyl	1·96	0·77	2·5	2·6

The theory which has been described thus accounts, not only for the main differences between one alcohol and another, but also for the variation of the activity coefficients

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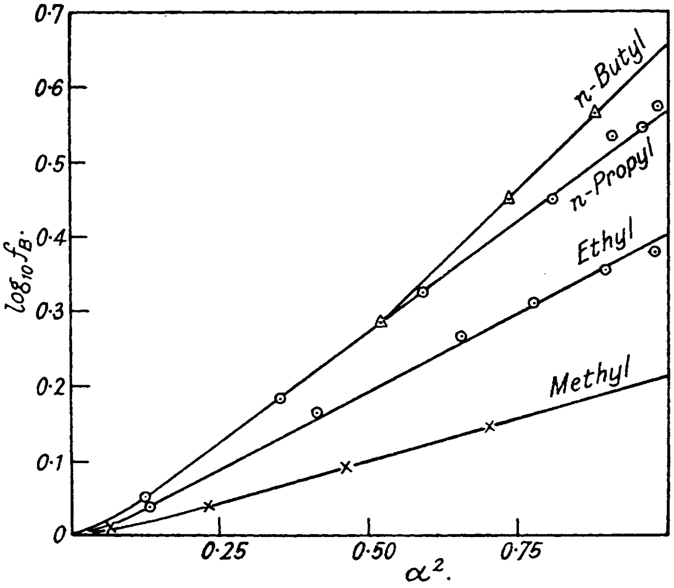
* In Table I as $\log f^0_{A(B)}$, $\log f^0_{B(A)}$.

over the greater part of the range of concentration. The divergences from the equations which occur in dilute aqueous solutions may be due to the failure of the assumption of an entirely random distribution and orientation of molecules in these solutions. The effect of orientation, if it occurs, must be to reduce the interfacial energy. It has been assumed for simplicity that the water molecule has a homogeneous surface, but it may well be that the interfacial energy between it and an alcohol molecule is least for some particular orientation. The possibility of complete orientation of those water molecules which are in contact with alcohol is greatest in dilute solutions, and as the proportion of alcohol increases, it becomes increasingly difficult. For example, in a solution containing equal numbers of water and alcohol molecules, each water molecule must be in contact with several alcohol molecules, and if the orientation is right for one it will probably be wrong for the others. In such solutions we might expect to find, as we have shown to be the case, that the assumption of random orientation and distribution is fairly satisfactory.

FIG. 5.

Logarithm of activity coefficients of water plotted against a^2.



There is, however, another possibility, *viz.*, that the deviation in dilute solutions is due to an increasing " association " of water molecules as the alcohol content diminishes. Association of water molecules will only occur if the intermolecular energy is thereby reduced, and the cohesive energy between the associated units will be less than the average value of that between molecules. Less work may therefore be required to make a cavity in " associated " than in " dispersed " water, provided that the associated groups are not split up, and in such a case γ_B and ϕ will be smaller when association has taken place. Since the association of water molecules might be regarded as due to their mutual orientation, further progress would appear to require a closer study of molecular orientation in liquids and its effects.

SUMMARY.

1. Determinations of the partial vapour pressures of aqueous solutions of methyl, *n*-propyl, and *n*-butyl alcohols, of the mutual miscibility of butyl alcohol and water, and of the solubilities of the normal aliphatic alcohols from C_5 to C_8, at 25°, are described.

2. The activity coefficients at infinite dilution in water of the alcohols, beginning with ethyl alcohol, increases in an approximately constant ratio for each additional CH_2 group. The activity coefficients of water in the alcohols increase in gradually diminishing ratios as we pass up the series.

3. A modified form of Langmuir's theory of solutions is presented, and applied to these solutions. It is capable of accounting for the main features of the differences between one alcohol and another, and for the variation of the activity coefficients of the lower alcohols with concentration, except in solutions containing a large proportion of water. In these solutions marked deviations from the equations occur which are attributed either to orientation of the water round the alcohol molecules, or to the association of water.

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