

58. *The Solubility of Non-electrolytes. Part I. The Free Energy of Hydration of Some Aliphatic Alcohols.*

By J. A. V. BUTLER, C. N. RAMCHANDANI, and D. W. THOMSON.

THE factors which determine the free energies of solutions may be divided into two groups : (i) those operating in such dilute solutions that there is no interaction between solute molecules, (ii) additional factors in more concentrated solutions where this interaction cannot be ignored. These factors may be separated thermodynamically by expressing the free energy of a solute by

$$\bar{F} = \bar{F}^\circ + RT \log Nf' \quad \dots \quad (1)$$

where \bar{F}° is taken as a constant for a given solvent and the variation of the free energy with the concentration (in so far as it differs from $\bar{F} = \bar{F}^\circ + RT \log N$) is expressed by means of the activity coefficient f' , which is taken as unity when the molar fraction $N \rightarrow 0$. Up to the present, more attention has been given to the variation of the activity coefficients with concentration than to the elucidation of the factors determining \bar{F}° . Of the factors determining solubility, the latter is usually the more important term, particularly in the case of slightly soluble substances. Moreover, since this quantity depends only on the interactions between the solute molecule and the solvent molecules in its vicinity, it presents a more favourable case for theoretical interpretation. In this series of papers we propose to determine \bar{F}° for a variety of solutes and solvents, the present paper being concerned with the aliphatic alcohols in aqueous solution.

It is necessary to refer \bar{F}° to some constant standard state for each substance. In a previous investigation (J., 1933, 674) we determined for a number of these alcohols the quantity

$$\bar{F}^\circ - F^\circ_2 = RT \log (p/p^\circ N) = RT \log f^\circ \quad \dots \quad (2)$$

where F_2° is the free energy of the substance as a pure liquid, having the vapour pressure p° , p is its partial pressure over a very dilute solution of molar fraction N , and f° is the activity coefficient in such a solution referred to the pure liquid, in which the value is unity. This quantity is not, however, well adapted for theoretical interpretation, since it involves a consideration of the state of the substance as a pure liquid, itself a complex state. It is preferable to take the gaseous state as the standard of reference. Thus, if F_g° is the molar free energy of a substance in the vapour at unit pressure (1 mm. Hg), its free energy at a pressure p is

$$\bar{F} = F_g^\circ + RT \log p \dots \dots \dots (3)$$

so that if p is the partial pressure of the solute over a solution of molar fraction N , which is so dilute that $f' = 1$, we obtain by equating (1) and (3), the following quantity which may be called the free energy of hydration of the solute;

$$\bar{F}^\circ - F_g^\circ = RT \log (p/N) \dots \dots \dots (4)$$

The ratio p/N , which is in effect the limiting value at small concentrations of the distribution ratio of the substance between the vapour and the solvent, may be determined by one of the following two methods according to whether the miscibility is high or not. (1) By direct measurement of the partial vapour pressure of the solute in a sufficiently dilute solution, or by extrapolation from the values of more concentrated solutions. Values for the two lowest normal alcohols can be obtained from the data previously given (*loc. cit.*). In the case of *n*-propyl and *n*-butyl alcohols, insufficient points were available for an accurate extrapolation, and measurements of this ratio were made with dilute solutions of these alcohols, and also for *isopropyl*, three isomeric butyl, and four amyl alcohols. (2) When the miscibility is low, the ratio (p/N) for dilute solutions is given by p°/N_s , where p° is the vapour pressure of the pure solute and N_s its molar fraction in the (dilute) saturated solution. This is exact if the solute is a solid, and may be taken as reasonably accurate in the case of liquids of small mutual miscibility; N_s has been determined for the four normal alcohols C_5 — C_8 . In order to use these values, it was necessary to know the vapour pressures of the alcohols at 25° . We have therefore determined these over a range of temperature, from which an extrapolation to 25° could be made. Since the recorded vapour pressures of alcohols are very incomplete, it appeared to be useful to determine those of other alcohols, of which we had purified specimens.

EXPERIMENTAL.

Determination of the Vapour Pressures.—The method was a modification of the isotenscope method of Smith and Menzies (*J. Amer. Chem. Soc.*, 1910, **32**, 1412). The liquid was contained in a 5-c.c. bulb with a small manometer attached. This was connected through a ground joint (with mercury seal) to a vertical condenser, and a large reservoir, provided with a mercury manometer and an efficient pump. The small manometer contained some of the bulb liquid, and the method consisted in observing the reservoir pressure and the temperature of the bulb when the levels of liquid in the two arms of the small manometer were the same. The small bulb and manometer were immersed in a well-lagged glycerol-bath provided with an electric heater and a very efficient stirrer. It was found possible by manual handling for one experimenter to keep the temperature of the bulb constant to $\pm 0.01^\circ$ below 100° and to $\pm 0.02^\circ$ above 100° , while the other adjusted the pressure in the reservoir to give equal levels in the small manometer. The thermometers used were calibrated against standards certified by the N.P.L. The barometer was new, and was checked against the readings of the local meteorological station, a correction being made for the difference of altitude. The levels of the large manometer were read with a cathetometer reading to 0.05 mm. The method depends on the bulb being initially free from air. At the beginning of the experiment the pressure in the apparatus was reduced so that vapour from the bulb bubbled through the liquid of the small manometer and carried with it the dissolved air. This was continued until a concordant series of vapour pressures was obtained both at increasing and at decreasing temperatures.

Materials.—The higher alcohols were the specimens used in the solubility determinations. Before use they were dried and redistilled. The other alcohols were the purest B.D.H. prepar-

ations; these were refluxed over lime for 18 hours, and fractionated through a long column. The fractions employed distilled within a range of less than 0.2°. The ranges within which the fractions used were collected are given below, together with other physical constants. The b. p.'s (corr.) were obtained from observations in the vapour-pressure apparatus of the temperature corresponding to atmospheric pressure, with a correction to 760 mm. from the slope of the vapour-pressure curve.

Alcohol.	B. p./mm.	B. p./760 mm.	$D_4^{25^\circ}$.	$n_D^{20^\circ}$.
<i>iso</i> Propyl	82.01—82.03/748.4	82.39°	0.7812 ₆	1.3688 ₆
<i>n</i> -Butyl	117.16—117.26/742.4	117.71	0.8059 ₃	1.3998 ₂
<i>iso</i> Butyl	107.87—107.91/767.1	107.89	0.7983 ₃	1.3960 ₃
<i>sec.</i> -Butyl.....	99.58—99.70/755.3	99.95	0.8029 ₉	1.3984 ₆
<i>tert.</i> -Butyl *.....	81.77—81.87/733.4	82.75	—	—
<i>n</i> -Amyl.....	137.1—137.2/747.4	137.75	0.8125 ₃	1.4111 ₃
<i>iso</i> Amyl	131.15—131.35/761.2	131.35	0.8102 ₂	1.4096 ₄
<i>sec.</i> -Amyl.....	120.26—120.29/775.3	119.89	0.8052 ₅	1.4178 ₇
<i>tert.</i> -Amyl.....	101.98—102.2/768.3	101.9	0.8059 ₉	1.4058 ₀
<i>n</i> -Hexyl	64.4—64.5/9	155.7	0.8183 ₅	1.4182 ₇
<i>n</i> -Heptyl	76.7—76.8/9	175.6	0.8205 ₃	1.4252 ₇
<i>n</i> -Octyl.....	89.1—89.2/9	194.5	0.8232 ₂	1.4295 ₇

* M. p. 25.5°.

Results.—The values obtained are given in Table I. Of these, agreement with previously recorded data is shown in four cases, *viz.*, *n*-butyl alcohol (Kahlbaum, *Z. physikal. Chem.*, 1898, **26**, 577); *isobutyl* and *isoamyl* alcohols (Schmidt, *ibid.*, 1891, **3**, 628; Richardson, *J.*, 1886, **49**, 761), and *tert.*-butyl alcohol (Parks and Burton, *J. Amer. Chem. Soc.*, 1928, **50**, 24). The results for *n*-amyl alcohol are not in agreement with those recorded by Grassi (*Nuovo Cim.*, 1888, **23**, 109), while in the remaining six cases no pressures over a range of temperature have been recorded. Table II gives the constants of the extrapolation formula

$$\log_{10} p = A - B/T - C \log_{10} T,$$

which are required to reproduce the experimental figures. The average deviations (%) in either direction between the experimental values and those calculated by this formula are given under Δ , and ΔH_{298° is the calculated latent heat of vaporisation at 25°. The values for the higher-boiling alcohols at 25°, which are given in parentheses in Table I, were obtained from these formulæ.

TABLE I.

Vapour pressures of aliphatic alcohols (mm. Hg).

<i>T</i> (K).	<i>n</i> - Butyl.	<i>iso</i> - Butyl.	<i>sec.</i> - Butyl.	<i>tert.</i> - Butyl.	<i>n</i> - Amyl.	<i>iso</i> - Amyl.	<i>sec.</i> - Amyl.	<i>tert.</i> - Amyl.	<i>n</i> - Hexyl.	<i>n</i> - Heptyl.	<i>n</i> - Octyl.
298.13°	6.78	11.56	17.15	(42.41)*	(2.50)	3.11	6.03	16.72	(0.719)	(0.224)	(0.083)
303.15	9.57	16.47	24.54	58.15	—	4.61	8.79	23.30	—	—	—
308.18	13.50	22.39	33.30	78.18	—	6.75	12.44	32.0	—	—	—
323.23	34.45	55.62	80.74	177.8	—	18.09	32.40	77.14	—	—	—
333.27	60.69	95.84	138.4	291.4	26.01	33.78	57.92	129.8	9.75	3.79	1.65
343.45	103.0	159.7	224.1	462.4	46.15	59.27	99.12	211.4	17.74	7.48	3.31
348.58	—	—	—	547.0	—	—	—	—	—	—	—
353.74	168.5	256.4	355.2	705.9	77.74	99.52	161.8	332.8	31.60	14.35	6.68
363.99	266.6	397.8	543.1	—	125.8	160.6	255.5	505.5	54.57	25.73	11.92
374.32	408.3	600.7	—	—	198.0	251.5	390.4	—	90.01	44.12	21.51
383.35	578.6	—	—	—	286.9	361.2	550.2	—	135.1	67.96	33.42
393.71	—	—	—	—	424.1	532.3	—	—	207.2	107.2	54.02
404.04	—	—	—	—	611.9	—	—	—	309.8	163.6	85.43
414.83	—	—	—	—	—	—	—	—	456.8	246.5	132.63
425.93	—	—	—	—	—	—	—	—	659.8	364.5	201.45

* Solid at 25°.

The Partial Pressures of the Alcohols in Dilute Aqueous Solutions.—We used the air-bubbling method previously employed (Butler, Thomson, and MacLennan, *loc. cit.*). In sufficiently dilute solutions, it is, however, unnecessary to determine the total weight of vapour carried over by a measured volume of air. Assuming that Raoult's law ($p_1 = p_1^\circ N_1$) holds for the solvent, the partial pressure of the solute can be determined by the observation of the relative proportions of the solute and solvent in the vapour only. For, if n_1 and n_2 are the relative molar concentrations of the solvent and solute in the condensate of the vapour, and p_2 is the partial pressure of the solute, we have $n_2/n_1 = p_2/p_1^\circ N_1$, from which p_2 can be determined.

TABLE II.
 Constants of the extrapolation formulae.

Alcohol.	A.	B.	C.	Δ , %.	ΔH_{298° .
<i>n</i> -Butyl	40·2105	4100	10·35	0·12	12,630
<i>iso</i> Butyl	43·5513	4185	11·50	0·3	12,340
<i>sec.</i> -Butyl	43·4800	4110	11·50	0·5	12,000
<i>tert.</i> -Butyl	43·2834	3935	11·50	0·12	11,200
<i>n</i> -Amyl	46·4925	4580	12·42	0·2	13,600
<i>iso</i> Amyl	51·5074	5120	16·10	0·6	13,900
<i>sec.</i> -Amyl	48·4849	4550	13·11	0·6	13,060
<i>tert.</i> -Amyl.....	47·4492	4280	12·88	0·15	11,960
<i>n</i> -Hexyl	51·0030	5068	13·80	0·4	15,020
<i>n</i> -Heptyl	56·1972	5580	15·41	1·5	16,410
<i>n</i> -Octyl	65·2106	6190	18·40	1·0	17,430

The compositions of the condensates were determined by interferometric methods, at least two reasonably concordant values being obtained in every case. The results are given in Table III, where N is the molar fraction of the solute in the solution, x the composition of the condensate (wt. %) at 25°, and p its partial pressure (in mm. Hg).

TABLE III.

Alcohol.	$N \times 10^3$.	x .	p .	p/N .	Alcohol.	$N \times 10^3$.	x .	p .	p/N .
<i>n</i> -Propyl	0·929	3·66	0·270	291	<i>tert.</i> -Butyl ...	0·937	7·55	0·471	503
<i>iso</i> Propyl	0·986	4·49	0·334	339	<i>n</i> -Amyl	0·468	4·87*	0·249	532
<i>n</i> -Butyl	0·992	5·81	0·356	359	<i>iso</i> Amyl	0·506	5·83*	0·301	593
<i>iso</i> Butyl	1·143	9·00*	0·571	499	<i>sec.</i> -Amyl ...	0·496	5·98*	0·309	622
<i>sec.</i> -Butyl ...	0·959	6·68	0·413	431	<i>tert.</i> -Amyl ...	1·033	11·03*	0·601	582

* In these cases the condensate was in two phases and the composition was determined after dilution with sufficient water to give a homogeneous solution.

The results of the investigation are assembled in Table IV. The distribution ratios (p/N) (col. 4) are those obtained by direct measurement of the partial pressure of very dilute solutions, except in the case of methyl and ethyl alcohols, which are obtained by extrapolation from the values at higher concentrations, and those marked with an asterisk, which are derived from the solubility. The values of $f^\circ = (p/p^\circ N)$ (col. 4) are calculated from cols. 1 and 3. The values for the lower alcohols are somewhat greater than those given in the previous paper, because the present measurements of very dilute solutions show that, in making the extrapolation of $p/p^\circ N$ from $N = 0\cdot01$ to zero concentration, too great an allowance was previously made for the flattening of the curve in dilute solutions.

The accuracy of the vapour-pressure determinations depends on the correctness of the condensate composition. The greatest variations of the latter observed in repeated experiments with the same or similar solutions amounted to about 10% but in most cases, particularly when

TABLE IV.

Distribution ratios (p/N) of aliphatic alcohols between the vapour and dilute aqueous solutions at 25°, and related quantities.

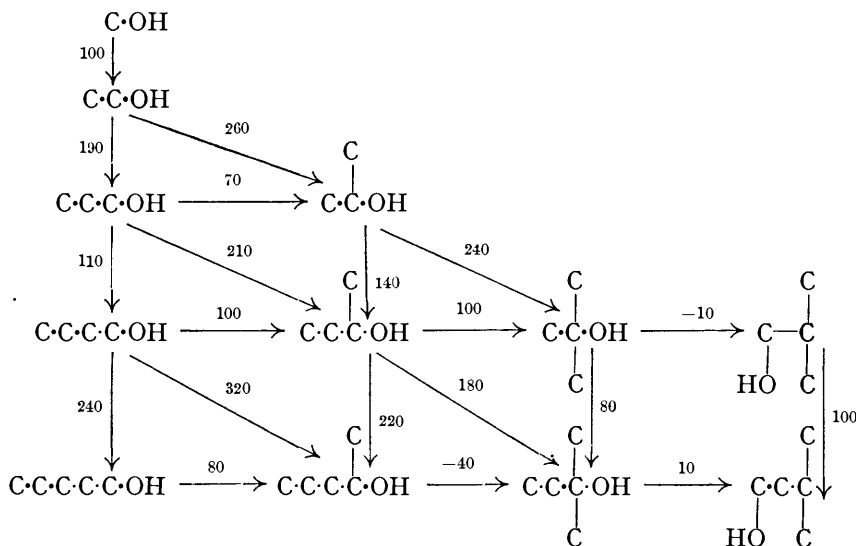
Alcohol.	p° .	$1/N_*$.	p/N .	$p/p^\circ N$.	$RT \log p/N$.
Methyl	122·2	—	184	1·51	3090
Ethyl	59·0	—	218	3·69	3190
<i>n</i> -Propyl	20·1	—	291	14·4	3380
<i>iso</i> Propyl	44·0	—	339	7·7	3450
<i>n</i> -Butyl	6·78	53·1	360 *	—	—
	—	—	359	52·9	3490
<i>iso</i> Butyl	11·56	—	499	43·2	3680
<i>sec.</i> -Butyl	17·15	—	431	25·1	3590
<i>tert.</i> -Butyl	42·41	—	503	11·8	3690
<i>n</i> -Amyl	2·50	219	547 *	—	—
	—	—	532	214	3730
<i>iso</i> Amyl	3·11	—	593	191	3784
<i>sec.</i> -Amyl	6·03	—	622	103	3812
<i>tert.</i> -Amyl.....	16·72	—	582	35	3773
<i>n</i> -Hexyl	0·719	903	649 *	903 *	3840 *
<i>n</i> -Heptyl	0·224	3,560	798 *	3,560 *	3960 *
<i>n</i> -Octyl	0·083	12,300	1020 *	12,300 *	4110 *

dilution of the condensate was unnecessary, a much smaller variation was obtained. An uncertainty of 5% in the partial pressure corresponds to about ± 30 cal. in $\bar{F}^\circ - F_g^\circ$. Account being taken of the numerous instrumental factors which enter into the determinations, an error of ± 40 cal. may be allowed in individual cases.

DISCUSSION.

It was shown in the previous investigation that in the series of normal aliphatic alcohols the quantity $\bar{F}^\circ - F_g^\circ = RT \log (p/p^\circ N)$ increases by an approximately constant increment for each additional methylene group. That a large part of this increment is due to the factor p° can be seen from Fig. 1, where the differences of the values of $-RT \log p^\circ$ and of $RT \log (p/p^\circ N)$ from the values of methyl alcohol are plotted for the normal alcohols against the number of carbon atoms. The average increment of $RT \log (p/p^\circ N)$ between C_2 and C_8 is about 800 cal., while the average increment of $-RT \log p^\circ$ is 640 cal., leaving about 160 cal. for the increment of $RT \log p/N$. The experimental values of the latter are shown on a larger scale in Fig. 2. The first interval between C_1 and C_2 is abnormally small, but between C_2 and C_8 the average increment is 165 cal. Since this quantity depends only on the interaction of the isolated alcohol molecule with water, it is clear that each methylene group of the normal alcohols makes a definite contribution to the free energy of this interaction. Although none of the values deviates from the line representing the average increment by more than the possible error, the alcohols above C_5 taken as a group show a somewhat smaller average increment than those below. This might possibly be due to the completion of a ring at this point, but the difference is not very great and the accuracy at present obtainable is not sufficient to make it possible to decide if this effect is real.

The differences of p/N between the isomeric alcohols are not greater in some cases than the possible experimental error of individual determinations. Nevertheless, certain regularities can be detected, as can be seen from the differences of $\bar{F}^\circ - F_g^\circ$ shown in the following scheme.



In the alcohols in which the carbon atoms are arranged in a straight chain, the displacement of the hydroxyl group from the terminal carbon to the second (giving a secondary alcohol) causes an increase in $\bar{F}^\circ - F_g^\circ$ of about 100 cal.; *i.e.*, although the addition of a methylene group at the end of a straight chain gives an average increment of 165 cal., yet its addition to the α -carbon atom gives an increment of about 260 cal. A further

increment of the same magnitude is observed when a second methylene group is added in the α -position, giving a tertiary alcohol.

FIG. 1.

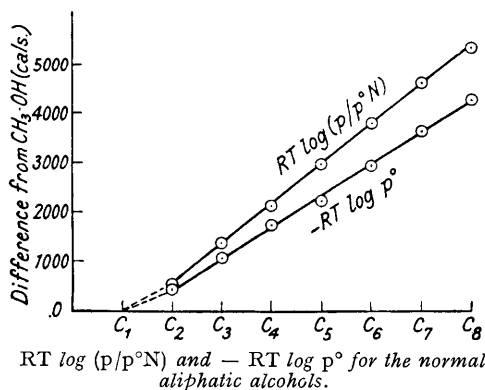
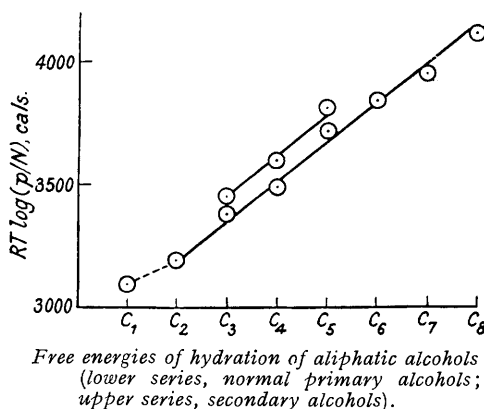
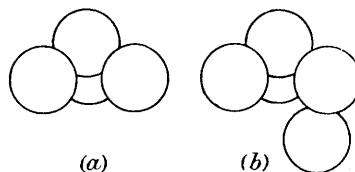


FIG. 2.



The alcohols with a branched carbon chain form a group by themselves. The two butyl alcohols having the nucleus (a), Fig. 3, and the two amyl alcohols with the nucleus (b) have nearly the same value of p/N , *i.e.*, in both cases it appears to be immaterial to which carbon atom the hydroxyl group is attached. This can be understood when the spatial arrangement of the carbon atoms in these compounds is taken into account: those in the group (a) are arranged in a pyramid, and it can be seen that a hydroxyl group attached to any one of the carbon atoms is somewhat similarly related to the other three. Similarly, in group (b), the three carbons attached to one carbon atom form a pyramid, while the fourth has freedom of movement, but in aqueous solution its position of minimum energy is under the pyramid, forming a somewhat asymmetric hexahedron. A hydroxyl group attached to either of these carbon atoms will now be somewhat similarly related to the others, irrespective of its position.

FIG. 3.



The origin of these effects will be discussed in another paper.

SUMMARY.

1. Measurements have been made of (1) the vapour pressures of eleven aliphatic alcohols over a range of temperature; (2) the partial vapour pressures in very dilute aqueous solution ($N = ca. 10^{-3}$) of ten aliphatic alcohols at 25° .

2. From these measurements, together with data previously published, we obtain values of the free energy of hydration ($\bar{F}^\circ - F_g^\circ = RT \log p/N$) at 25° of the normal alcohols from C_1 to C_8 , of isopropyl, three isomeric butyl, and three isomeric amyl alcohols.

3. It is shown that in the series of normal alcohols, of the increment of 800 cals. for each additional methylene group previously found in the quantity $RT \log (p/p^\circ N)$, ($p/p^\circ N$ being the activity coefficient of the alcohol in dilute aqueous solution referred to the pure liquid), about 640 cals. is accounted for by the variation of $RT \log p^\circ$, while the increment of $RT \log (p/N)$ is about 160 cals.

4. The isomeric alcohols show small, but apparently significant, differences the nature of which is discussed.

We thank the Committee of the Earl of Moray Endowment for a grant.

KING'S BUILDINGS, WEST MAINS ROAD, EDINBURGH.

[Received, December 12th, 1934.]