270. *Viscosity and Molecular Association. Part II. A Relationship between Viscosity and Vapour Pressure of Associated Liquids.*

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A general equation is proposed connecting the viscosity of an associated liquid with vapour pressure, and degrees of association of a number of alcohols tabulated as functions of temperature. Stable association complexes seem to be formed at low temperatures.

Part I (preceding paper) dealt with those substances exhibiting a linear relationship between log $\phi\sqrt{d}$ and log p, *i.e.*, with substances having sensibly constant degrees of association over the temperature ranges examined. However, for most alcohols, the degree of association decreases with rising temperature and vapour pressure and we may then write

$$\gamma = 4{\cdot}545aE - h/(E - h) \qquad (1)$$

where a and E are now functions of the vapour pressure such that

$$a = \mathrm{d} \log \phi\sqrt{d}/\mathrm{d} \log p$$
$$E = -\boldsymbol{R}\, \mathrm{d} \log_e p/\mathrm{d}(1/T)$$

A direct determination of the slopes of the log $\phi\sqrt{d}$–log p curves from the recorded viscosity and vapour-pressure data was impracticable because these were not sufficiently accurate. However, it has been found that the η–p behaviour of associated substances is in good agreement with an equation of the form

$$\eta\sqrt{v} = A/p^a + D/p^d \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where D and d are additional constants.

Now $d > a$, so the second term at sufficiently high vapour pressures tends to become very small in comparison with the first; (1) then approximates to the equation $\log \phi\sqrt{d} = b + a \log p$ (see Part I). It seems reasonable to suppose that at a sufficiently high temperature, the substance becomes virtually non-associated, or, more accurately, the molecular weight of the substance in the liquid state becomes equal to that in the vapour state. The value of a in (2) was therefore assumed to be 0·220, and we then get

$$\eta\sqrt{v} = A/p^{0\cdot220} + D/p^d \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

or

$$\log[\eta\sqrt{v}p^{0\cdot220} - A] = \log D - (d - 0\cdot220) \log p$$

The equation was solved by selecting a value of A such that the plot of log $[\eta\sqrt{v}p^{0\cdot220} - A]$ against log p was the nearest approach to linear; d was then read off from the slope, and a best, mean value of D taken from $D = p^d\,[\eta\sqrt{v} - A/p^{0\cdot220}]$. In this way, A could be determined with a dependability of only $\sim \pm$ 10%; d values on the other hand are probably reliable to $\sim \pm$ 2%.

Values of A, D, and d so determined are tabulated below, together with the mean deviations between the experimental values of $\eta\sqrt{v}$ and those calculated from (3). A typical case is that of 2-methylpentan-3-ol. The higher average errors shown by certain of the other alcohols are largely due to large errors in one or two of the individual measurements and are not due to any ascertainable departure from (2).

Temp., t.	p, mm.	$\eta\sqrt{v}$, expt.	$\eta\sqrt{v}$, calc.	Error, %.	Temp., t.	p, mm.	$\eta\sqrt{v}$, exptl.	$\eta\sqrt{v}$, calc.	Error, %.
25°	6·0 (5·07)	40·18	39·80	+0·9	85°	163·0	6·744	6·749	−0·1
35	10·5 (10·30)	26·64	26·72	−0·3	95	247·0	5·594	5·638	−0·8
45	20·0 (19·86)	18·69	18·75	−0·3	105	364·0	4·754	4·803	−1·0
55	36·0	13·80	13·79	+0·1	115	520·0	4·161	4·168	−0·2
65	63·0	10·48	10·46	+0·2	125	719·0	3·715	3·685	+0·8
75	103·8	8·287	8·272	+0·2			Mean error = 0·4%		

As in Part I, the vapour pressures given in parentheses are those calculated from published p–T equations. In general, all measured vapour pressures below 30 mm. have been judged insufficiently accurate, and values so calculated have been used.

Substance.*	A.	D.	d.	Error, %.	$\eta_c\sqrt{v_c}$.	Error, %.	Temp. range.
4-Methylpentan-1-ol	6·00	48·0	0·430	0·8	1·208	3·8	25—145°
3-Methylpentan-1-ol	7·00	51·3	0·460	0·2	1·188	5·4	25—145
Hexan-2-ol	10·00	52·0	0·535	0·6	1·259	0·2	25—125
2-Methyl pentan-2-ol	10·00	58·3	0·553	1·3	1·245	0·9	25—115
2-Methylpentan-1-ol	10·00	66·8	0·557	0·6	1·265	0·7	35—135
3-Methylpentan-2-ol	10·00	77·5	0·590	0·4	1·227	2·3	35—125
2-Ethylbutan-1-ol	10·00	90·0	0·608	0·7	1·220	2·9	25—145
2-Methylpentan-3-ol	10·00	93·8	0·647	0·4	1·167	7·1	25—125
2 : 2-Dimethylbutan-1-ol	12·00	178·0	0·674	1·5	1·430	13·8	25—135
4-Methylpentan-2-ol	11·00	113·2	0·678	0·9	1·257	0·1	25—125
Hexan-3-ol	11·00	117·9	0·724	0·8	1·220	2·9	35—125
3-Methylpentan-3-ol	13·00	231·0	0·820	0·5	1·409	12·2	35—115
2 : 3-Dimethylbutan-2-ol	15·00	278·4	0·828	0·5	1·625	29·4	25—115
tert.-Butyl alcohol	12·00	918·0	0·827	0·8	1·359	8·2	30— 80
tert.-Amyl alcohol	12·00	273·0	0·724	1·2	1·376	9·6	0—100
Mean values	—	—	—	0·7	1·258	4·4	—

* p_c = 37·8 atm. for all except *tert.*-butyl alcohol (46·3) and *tert.*-amyl alcohol (42·0), as calculated in Part I.

References.—Viscosity. For last two alcohols, Thorpe and Rodger, *Phil. Trans.*, 1894, **185**, 397; 1897, **189**, 71; for others, Hovorka, Lankelma, *et al.*, *J. Amer. Chem. Soc.*, 1933, **55**, 4820; 1938, **60**, 820; 1940, **62**, 187, 1096, 2372; 1941, **63**, 1097.

Vapour pressure. For 14th alcohol, Parks and Barton, *ibid.*, 1928, **50**, 25; for last, Butler, Ramchandani, and Thomson, *J.*, 1935, 280; for others, Hovorka, Lankelma, *et al.*, *locc. cit.*

Equation (4) (p. 1353) applied to the data for *iso*propyl, *iso*butyl, *iso*amyl, and octyl alcohols leads to values of $\eta_c\sqrt{v_c}$ much lower than 1·256 thereby implying that, if the log $\phi\sqrt{d}$–log p plots continued linear beyond the ranges investigated, these alcohols are much less viscous at their respective critical temperatures than normal substances. But it is possible that at higher temperatures, the degree of association decreases, the plot ceases to be linear, and they become increasingly less viscous at a lower rate than previously, thus leading to normal or at least more normal values of $\eta_c\sqrt{v_c}$. Although there are no experimental data to justify this view, it is noteworthy that for alcohols already showing such a diminution in slope, (3) leads to a mean value of $\eta_c\sqrt{v_c}$ virtually identical with that for normal substances. The case of 2 : 3-dimethylbutan-2-ol seems exceptional and has therefore been omitted in calculating the averages.

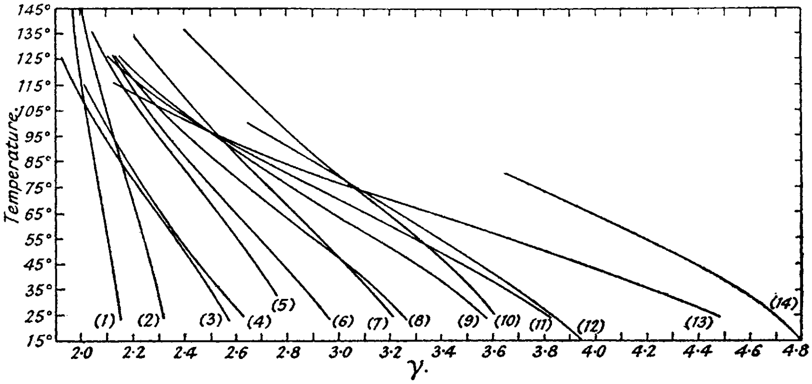
From (1) we get

$$a = \frac{\mathrm{d}\log\phi\sqrt{d}}{\mathrm{d}\log p} = \frac{0{\cdot}220A}{p^{0{\cdot}220}} + \frac{dD}{p^{d}} \bigg/ \frac{A}{p^{0{\cdot}220}} + \frac{D}{p^{d}}$$

Thus γ may be calculated from (1), it being assumed as before that $h = 3800$ cals.

The vapour-pressure data used in this paper have been fitted by the respective experimenters to the Dupré–Kirchoff equation, *viz.*, $\log p = F + G/T + H \log T$, so that $E = -\boldsymbol{R}\, d \log_e p/\mathrm{d}(1/T) = 4{\cdot}571G - \boldsymbol{R}HT$.

FIG. 1.



(1) 4-*Methylpentan*-1-*ol*. (2) 3-*Methylpentan*-1-*ol*. (3) *Hexan*-2-*ol*.
(4) 2-*Methylpentan*-2-*ol*. (5) 2-*Methylpentan*-1-*ol*. (6) 3-*Methylpentan*-2-*ol*.
(7) 2-*Ethylbutan*-1-*ol*. (8) 2-*Methylpentan*-3-*ol*. (9) 4-*Methylpentan*-2-*ol*.
(10) 2 : 2-*Dimethylbutan*-1-*ol*. (11) *Hexan*-3-*ol*. (12) tert.-*Amyl alcohol*.
(13) 2 : 3-*Dimethylbutan*-2-*ol*. (14) tert.-*Butyl alcohol*.

This method of determining E is not free from objections for it assumes E to be a linear function of T, whereas the author has shown (*J.*, 1947, 822) that for normal substances at least it is sensibly constant at temperatures near and above the b. p. However, in the absence of a more reliable equation, the E values so determined have been taken as sufficiently accurate for the purpose in hand. In any case, it is clear from the form of (1) that small differences in E do not significantly affect the numerical value of γ, this being determined chiefly by the value of a.

The degrees of association of 12 isomeric hexanols over the experimental ranges of temperature are shown graphically in Fig. 1.

Inspection of (3) readily shows that at sufficiently low vapour pressures, the first term become negligible in comparison with the second, so that a becomes equal to d, a conclusion implying that at sufficiently low temperatures, the degrees of association become constant. Actually, such " ultimate " degrees of association (n) would be attained by the hexanols at vapour pressures of $\sim$ 0·001 mm., corresponding to temperatures of $\sim -50°$ (cf. Bondi, *J. Chem. Physics*, 1946, **14**, 591) (Fig. 2). The lower, branched-chain alcohols, *iso*propyl, *iso*butyl, and *iso*amyl, give (see Part 1) substantially linear plots of log $\phi\sqrt{d}$ against log p at temperatures of 0—100°, but presumably begin to dissociate at higher temperatures. Normal straight-chain alcohols, as previously stated, apparently give complexes stable right up to the critical point.

The numerical values of these ultimate degrees of association have been estimated by the following methods.

(1) By assuming that the given p–T equations hold down to $\sim -50°$, so that E may be

calculated even at such low temperatures. A figure is not given for 3-methylpentan-3-ol; the vapour-pressure data for this alcohol are such that E over the range 35—115° slightly decreases with fall in temperature, and the p–T equation given by the authors (*locc. cit.*) does not appear to be correct. It is very unlikely that E would further decrease at still lower temperatures.

(2) In an earlier paper (*loc. cit.*) it was shown that for a normal, non-associated liquid at temperatures not too removed from the b. p. (T_b°), we can write $E = 5{\cdot}093\ T_b \log_{10} 82{\cdot}07\ T_b$. Now for an associated substance, γ may increase with decrease in temperature and so necessitate a corresponding increase in E owing to the greater amount of heat used in breaking up the complex on evaporation. Therefore

$$n = 4{\cdot}545d - h/(E - h)$$

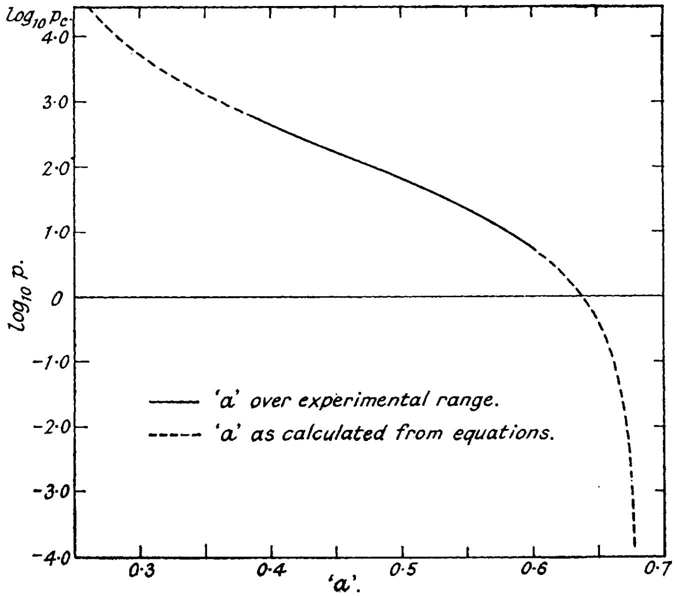
where

$$E = 5{\cdot}093\ T_b \log_{10} 82{\cdot}07\ T_b + (n - 1)h/n$$

Combination of these two equations gives a quadratic which may be solved for n.

In general, n determined by the first method is ~ 6% lower than that calculated by the second method. Both methods are, of course, only approximate, but in the author's opinion, the second method is the more reliable as well as the more convenient. It seems probable that the values of E at low temperatures involved in the first method are too high; *i.e.*, the Dupré–Kirchoff equation implies a more rapid increase in E than actually occurs—a conclusion which is certainly true in the neighbourhood of the b. p.

FIG. 2.



Values of n are tabulated below.

Substance.	Value of n by method: (1).	(2).	(3).	Mean.	h/100, cals.
4-Methylpentan-1-ol	2·2	2·4	2·4	2·3	23
3-Methylpentan-1-ol	2·4	2·6	2·5	2·5	39
Hexan-2-ol	2·8	3·1	3·2	3·0	34
2-Methylpentan-2-ol	3·0	3·3	3·5	3·3	28
2-Methylpentan-1-ol	3·0	3·2	3·3	3·2	41
3-Methylpentan-2-ol	3·2	3·5	3·6	3·4	37
2-Ethylbutan-1-ol	3·4	3·6	3·7	3·6	45
2-Methylpentan-3-ol	3·6	3·9	4·3	3·9	36
2 : 2-Dimethylbutan-1-ol	3·7	4·0	4·2	4·0	44
4-Methylpentan-2-ol	4·0	4·0	4·5	4·2	43
Hexan-3-ol	4·2	4·3	5·0	4·5	44
3-Methylpentan-3-ol	—	5·0	—	—	—
2 : 3-Dimethylbutan-2-ol	5·1	5·0	6·0	5·3	51
tert.-Butyl alcohol	4·9	5·2	5·3	5·1	62
tert.-Amyl alcohol	4·2	4·4	4·5	4·4	51
					Mean 41

Thermodynamical Evidence.—Let the ultimate association complex be denoted M_n. Then as the temperature rises we get a stepwise dissociation such that M_n is in equilibrium with M_{n-1}, M_{n-2}, ... M, the total concentration of the intermediate complexes gradually increasing. Let the degree of dissociation of the ultimate complex be Δ. If we may make the simplifying assumption that the equilibrium can be regarded as one between M_n and M, we have

$$\underset{(1-\Delta)}{M_n} \rightleftharpoons \underset{n\Delta}{nM} - (n-1)h \text{ cals.}$$

Therefore, total number of moles at equilibrium $= 1 + (n-1)\Delta$ and degree of association $= \gamma = n/[1 + (n-1)\Delta]$, whence $\Delta = (n-\gamma)/(n-1)\gamma$.

Suppose further that the system be treated as an ideal one—an assumption which cannot be far from the truth since we are dealing with a mixture of molecules of almost identical type. Then the equilibrium constant is given by

$$K = \left[\frac{\Delta}{V}\right]^n \left[\frac{V}{(1-\Delta)}\right] = \frac{\Delta^n}{V^{(n-1)}(1-\Delta)}$$

where V is the volume initially containing M_n.

Therefore, considering conditions at two different temperatures T_1 and T_2 where $T_1 > T_2$, we may write

$$\frac{K_1}{K_2} = \left[\frac{V_2}{V_1}\right]^{n-1} \left[\frac{1-\Delta_2}{1-\Delta_1}\right] \left[\frac{\Delta_1}{\Delta_2}\right]^n$$

Introducing γ in place of Δ, we have

$$\frac{K_1}{K_2} = \left[\frac{V_2}{V_1}\right]^{(n-1)} \left[\frac{1-1/\gamma_2}{1-1/\gamma_1}\right] \left[\frac{n/\gamma_1 - 1}{n/\gamma_2 - 1}\right]^n$$

Now it is clear that as the temperature falls from T_1, the first term decreases whereas the second increases. The effects of the two terms are therefore opposed, and in fact it is found that over the experimental ranges, the product of the two terms is approximately unity and varies only slightly between the two temperature extremes. It is then permissible to write

$$\log_{10} K_1/K_2 = n \log_{10} [n/\gamma_1 - 1)/(n/\gamma_2 - 1)]$$

But from the van't Hoff isochore, h being assumed to be independent of temperature, we get

$$\log_{10} K_1/K_2 = [(n-1)h/4{\cdot}571][1/T_2 - 1/T_1]$$

Therefore $$\log_{10}[(n/\gamma_1 - 1)/(n/\gamma_2 - 1)] = [(n-1)h/4{\cdot}571n][1/T_2 - 1/T_1]$$

or $$\log_{10} (n/\gamma - 1) = I' - (n-1)h/4{\cdot}571nT$$

or $$\log_{10} (1/\gamma - 1/n) = I + (1-n)h/4{\cdot}571nT \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where I' and I are constants.

If then the values of γ given above are correct, they might be expected to fit an equation of the form

$$\log_{10} (1/\gamma - 1/n) = I + J/T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where J is a constant. Further, the values of n and h should be in agreement with the values previously given.

In fact, by chosing suitable values of n, perfectly linear plots of log $(1/\gamma - 1/n)$ against $1/T$ were obtained; values of h were then calculated from the slopes.

A typical case is that of hexan-3-ol, degrees of association for which, calculated as above, are compared below with the values deduced from (1). The agreement is excellent when h is taken as 4420 cals. and n as 5·00.

Temp.	125°	115°	105°	95°	85°	75°	65°	55°	45°	35°	25°
γ from (1)	2·11	2·23	2·37	2·55	2·71	2·90	3·11	3·29	3·50	3·66	3·82
$\gamma_{\text{therm.}}$	2·11	2·25	2·40	2·56	2·73	2·91	3·09	3·28	3·46	3·65	3·85

A list of values of h and n is shown in the table on p. 1352. In general, n can be determined with an accuracy not exceeding ± 0·1 for those alcohols showing low degrees of association, to ± 0·3 for those highly associated. The values of h so determined are only very approximate, for they depend markedly on the selected value of n. Thus for hexan-3-ol, if $n = 4{\cdot}8$, $h = 4900$, and if $n = 5{\cdot}2$, $h = 4200$. Slight changes in the printed values of γ over the experimental ranges, such as could easily arise from probable errors in the calculation of E (see above), would also very appreciably alter the values of *h*, and to a lesser extent of *n*. It is then to be expected that large differences will exist between the values of *h* for the different alcohols; the average value however is 4100 cals.—not too different from the value 3800 cals. assumed in this paper. It is perhaps remarkable, in view of the nature of the approximations made, that the agreement is so good.

The thermodynamically derived values of *n* are $\sim$ 8% higher than those calculated by method (2) above, but the mean values are virtually identical with the latter. Also, in view of the uncertainties involved in the above thermodynamical argument, the latter figures are taken as the more reliable.

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