370. *Viscosity and Molecular Association. Part IV.* Association of Monohydric Alcohols and Some Hindered Phenols.*

By Leo H. Thomas and R. Meatyard.

The physical properties of a number of alcohols and phenols have been determined, and degrees of association of **36** lower monohydric alcohols and two hindered phenols have been evaluated. A correlation of extent of association with molecular structure is also presented.

By use of the nomenclature and methods of evaluation outlined in Part III, the values of the various constants expressing the viscosity and vapour-pressure behaviour of a number of alcohols not studied in earlier papers are given in Table 1. The values are based on our measurements of viscosity, density, and vapour pressure, with the exception of the densities of heptan-1-ol and octan-1-ol, which are from the literature.

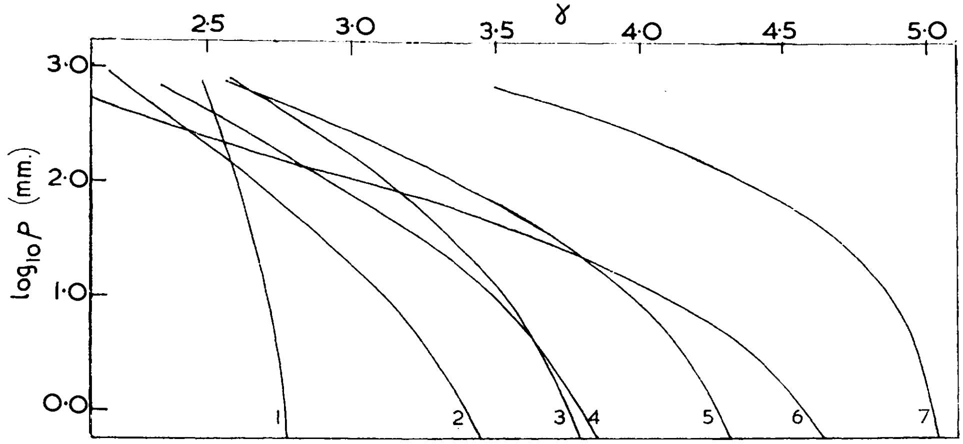

Fig. 1a. (1) 2-Methylbutan-1-ol. (2) Pentan-2-ol. (3) Butan-2-ol. (4) 3-Methylbutan-2-ol. (5) 2-Methylbutan-2-ol. (6) 2,3-Dimethylbutan-2-ol. (7) 2-Methylpropan-2-ol.

Degrees of association (γ) for the other alcohols have been given in Parts I and II (values previously reported for heptan-1-ol and octan-1-ol were, however, unreliable because of paucity of data). Refinements in procedure have necessitated re-evaluation in order that valid correlation of structure and extent of association may be attempted; the appropriate values of A, D, and d remain unaltered.

Data corresponding to a vapour pressure of 100 mm. mercury are printed in Table 2, and degrees of association (when not constant) for the appropriate experimental ranges (~5—760 mm.) are shown in the Figures. The hydrogen-bond enthalpies in the 8th column

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* Parts I—III, *J.*, 1948, 1345, 1349; 1960, 4906.

are those calculated as previously on the basis of " chain " polymers; those in the 9th column have been evaluated on the basis of " ring " polymers, as outlined in Part V (following paper). Those alcohols having values of γ independent of temperature at least over the experimental range, and therefore assumed to have attained their " ultimate "

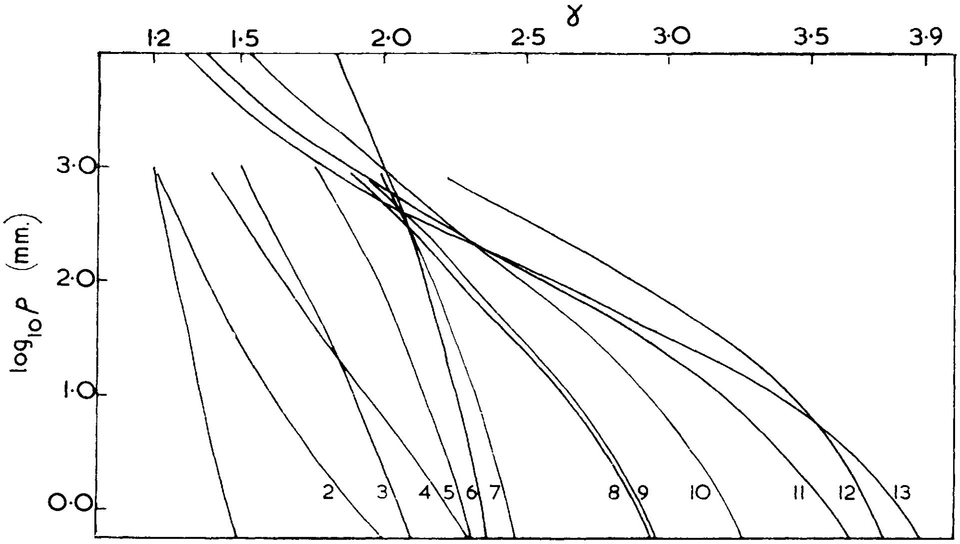

FIG. 1b. (1) 2,6-Di-t-butylphenol. (2) 5-Methyl-2-t-butylphenol. (3) Phenol. (4) *o*-Cresol. (5) Heptan-2-ol. (6) 4-Methylpentan-1-ol. (7) 3-Methylpentan-1-ol. (8) Hexan-2-ol. (9) 2-Methylpentan-1-ol. (10) 3-Methylpentan-2-ol. 11) 4-Methylpentan-2-ol. (12) 2,2-Dimethylbutan-1-ol. (13) Hexan-3-ol.

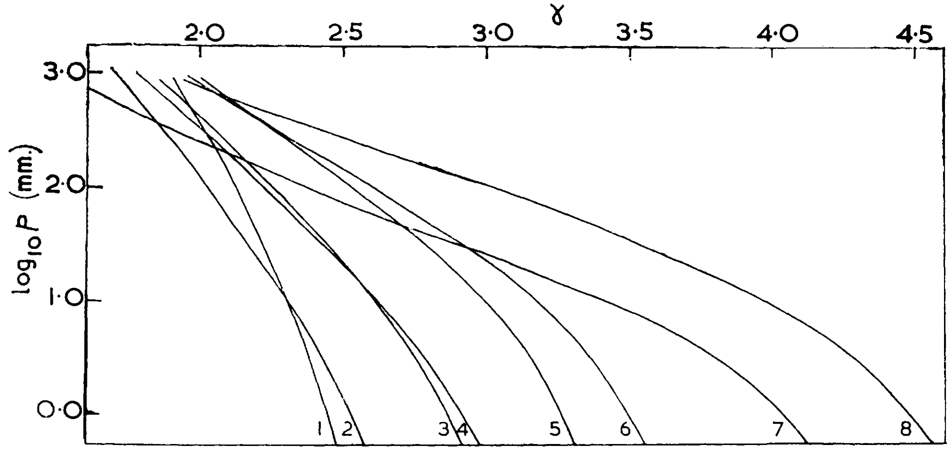

FIG. 1c. (1) Heptan-3-ol. (2) Heptan-4-ol. (3) 2-Methylpentan-2-ol. (4) 2-Methylhexan-2-ol. (5) 2-Ethylbutan-1-ol. (6) 2-Methylpentan-3-ol. (7) 2,4-Dimethylpentan-3-ol. (8) Pentan-3-ol.

degrees of association (Part II), are indicated in the Table by an asterisk. For such compounds, the plots of log T against log T_{benzene}, both temperatures corresponding to the same vapour pressure, are expected to be linear (Part III). The tabulated B values are then those derived by solution of eqn. 13 of Part III, and the mean deviations between the experimental temperatures for the range 10—760 mm. and those calculated from this

TABLE 1.

No.	Alcohol	A	D (or $10b$)	d (or a)	% devn.	Temp. range (°C)
I	Butan-2-ol	10·00	188	0·640	0·6	25—96
II	Pentan-1-ol	—	55·03	0·3820	0·5	41—130
III	Pentan-2-ol	10·00	95·5	0·600	0·6	25—113
IV	Pentan-3-ol	13·00	195	0·780	0·9	30—109
V	2-Methylbutan-1-ol	4·00	85·1	0·480	0·7	29—123
VI	3-Methylbutan-2-ol	12·00	162	0·660	0·7	18—107
XII	Heptan-1-ol	—	38·26	0·353	0·6	109—168
VII	Heptan-2-ol	7·00	36·6	0·460	0·1	60—150
VIII	Heptan-3-ol	6·00	39·5	0·470	0·6	54—145
IX	Heptan-4-ol	8·00	36·7	0·510	0·1	64—146
X	2-Methylhexan-2-ol	10·00	56·6	0·570	0·8	45—134
XI	2,4-Dimethylpentan-3-ol	12·00	103	0·780	0·8	48—133
XIII	Octan-1-ol	—	32·53	0·337	0·3	121—187
XIV	5-Methyl-2-t-butylphenol	12·00	12·0	0·520	0·4	90—190
XV	2,6-Di-t-butylphenol	12·00	8·2	0·390	0·3	91—190

η was measured in millipoises and p in mm.

TABLE 2.

Alcohol	n	F	B'	B_{100}	a_{100}	γ_{100}	$h/100$ (cal.) chain polymers	$h/100$ (cal.) ring polymers	$\gamma_{ult.}$	†	‡ $\eta_c \sqrt{v_c}$
Methanol	0	70·0	1·058	0·861	*0·264	1·47	54	27	1·5	0·3	1·22
Ethanol	0	100·0	1·046	0·813	*0·321	1·88	49	24	1·9	0·3	1·41
Propan-1-ol	1	128·4	1·028	0·790	*0·381	2·25	47	26	2·3	0·3	1·25
Propan-2-ol	0	130·0	1·040	0·794	*0·482	2·87	39	26	2·9	0·2	0·86
Butan-1-ol	2	156·1	1·011	0·789	*0·375	2·19	48	26	2·2	0·1	1·15
2-Methylpropan-1-ol	1	158·0	1·023	0·778	*0·476	2·85	43	28	2·8	0·1	0·97
Butan-2-ol	1	,,	,,	0·784	0·527	3·13	39	29	3·9		1·22
2-Methylpropan-2-ol	0	160·0	1·036	0·774	0·719	4·37	36	29	5·1		1·36
Penta-1-ol	3	183·0	0·996	0·798	*0·382	2·16	45	25	2·2	0·3	1·05
3-Methylbutan-1-ol	2	185·3	1·008	0·786	*0·405	2·36	47	27	2·4	0·1	1·00
2-Methylbutan-1-ol	,,	,,	,,	0·783	0·444	2·60	44	28	2·8		1·00
Pentan-2-ol	,,	,,	,,	0·785	0·457	2·67	42	30	3·6		1·21
Pentan-3-ol	,,	,,	,,	0·795	0·519	3·00	37	29	4·7		1·39
3-Methylbutan-2-ol	1	187·7	1·021	0·792	0·500	2·93	39	29	4·0		1·40
2-Methylbutan-2-ol	½	188·8	1·028	0·787	0·568	3·37	38	29	4·4		1·38
Hexan-1-ol	4	209·4	0·982	0·807	*0·377	2·08	43	23	2·1	0·1	1·02
4-Methylpentan-1-ol	3	212·0	0·994	0·797	0·378	2·14	47	28	2·5		1·21
3-Methylpentan-1-ol	,,	,,	,,	0·808	0·389	2·17	43	27	2·6		1·19
2-Methylpentan-1-ol	,,	,,	,,	0·817	0·417	2·31	39	27	3·2		1·27
2-Ethylbutan-1-ol	2	214·5	1·006	0·820	0·451	2·52	37	27	3·5		1·22
2,2-Dimethylbutan-1-ol	1½	215·9	1·013	0·820	0·514	2·89	34	26	3·9		1·43
Hexan-2-ol	3	212·0	0·994	0·786	0·393	2·26	47	32	3·2		1·31
Hexan-3-ol	,,	,,	,,	0·832	0·479	2·60	31	23	4·1		1·22
3-Methylpentan-2-ol	2	214·5	1·006	0·800	0·437	2·50	41	29	3·5		1·23
4-Methylpentan-2-ol	,,	,,	,,	0·840	0·474	2·58	31	23	3·8		1·26
2-Methylpentan-3-ol	,,	,,	,,	0·816	0·463	2·60	36	26	3·8		1·17
2-Methylpentan-2-ol	1½	215·9	1·013	0·836	0·406	2·24	35	24	3·2		1·24
3-Methylpentan-3-ol	,,	,,	,,	∝ 0·80	0·54	3·1	—	∝ 27	~5		—
2,3-Dimethylbutan-2-ol	½	218·7	1·026	0·836	0·540	3·01	31	24	4·8		1·62
Heptan-1-ol	5	235·2	0·970	0·804	*0·353	1·94	47	23	1·9	0·3	1·04
Heptan-2-ol	4	238·0	0·981	0·840	0·373	1·98	35	21	2·5		1·07
Heptan-3-ol	,,	,,	,,	0·815	0·389	2·13	40	23	2·6		0·96
Heptan-4-ol	,,	,,	,,	0·835	0·379	2·02	36	23	2·8		1·05
2-Methylhexan-2-ol	3½	239·5	0·987	0·820	0·405	2·22	37	26	3·3		1·27
2,4-Dimethylpentan-3-ol	2	243·8	1·005	0·850	0·441	2·37	30	23	4·4		1·30
Octan-1-ol	6	260·4	0·957	0·808	*0·337	1·81	48	24	1·8	0·2	1·06
5-Methyl-2-t-butylphenol	2½	321·5	0·972	0·897	0·281	1·38	37	24	2·8		—
2,6-Di-t-butylphenol	2	411·3	0·981	0·911	0·261	1·28	44	23	2·1		—

† Mean deviation (Part III, eqn. 13), in the approximate range from 10 mm. to b. p.

∝ The vapour pressures below 140 mm. appear to be seriously in error; the value of B_{100} quoted is calculated on the assumption that $h = 2700$ cal.

‡ For pentanol and higher alcohols, critical pressures have been calculated by Hertzog's method (*Ind. Eng. Chem.*, 1944, **36**, 997).

equation are shown in column 11. In no case is there significant departure from linearity, and the deviations probably lie within the limits of experimental error. For the remaining alcohols, B increases somewhat with rising temperature as expected, and values of B corresponding to a vapour pressure of 100 mm. have been calculated by numerical differentiation from the plot of log T against log T_{benzene}.

In their behaviour in the experimental regions studied, the alcohols fall into three groups: (*a*) Those having constant degrees of association, and showing a linear plot of log $\eta\sqrt{v}$ against log p which on extrapolation to critical conditions give values of log $n_c\sqrt{v_c}$ in reasonable agreement with the value for non-associated substances.[1] This applies to the straight-chain alcohols from methanol to butanol, the average value of $\eta_c\sqrt{v_c}$ being 1·26 (η in millipoises) compared with a mean value for non-associated substances of 1·26. Such behaviour implies that the association complexes are unusually stable and the alcohols therefore exhibit their ultimate degrees of association even at quite high temperatures. (*b*) Those showing variation in γ, but which still lead to normal $\eta_c\sqrt{v_c}$ values, *e.g.*, the mean $\eta_c\sqrt{v_c}$ value for 5 C_5 alcohols and 13 C_6 alcohols is 1·29. Variation in γ in the experimental range is of course allowed for by the nature of the η/p equation used (*i.e.*, eqn. 3, Part III). Such alcohols attain their ultimate degrees of association only at temperatures below those studied experimentally. (*c*) The lower branched-chain alcohols, isopropyl, isobutyl, and isopentyl, and also the higher straight-chain alcohols have linear plots of log $\eta\sqrt{v}$ against log p, but lead to values of $\eta_c\sqrt{v_c}$ significantly lower than 1·26. These alcohols have apparently attained their ultimate degrees of association under the experimental conditions but are partly dissociated at higher temperatures.

The Figures show values of γ over the experimental ranges, and also values extrapolated to lower vapour pressure (1 mm.), and, for a few cases, to higher vapour pressure. To a close approximation, γ differs from a only by an approximately constant factor so that the general form of the plot of a against log p (see Part II) is similar to that of γ against log p shown in Fig. 1.

By successive differentiation of eqn. 3 of Part III, and equation to zero it can be shown that $\mathrm{d}a/\mathrm{d}\log p$ is a maximum $[(d - 0{\cdot}220)^2/4]$ when $\log p = [1/(d - 0{\cdot}220)] \log (D/A)$, or when $a = (d + 0{\cdot}220)/2$. But since $\mathrm{d}\gamma/\mathrm{d}a$ is very nearly constant (see eqn. 4 of Part III; E/E' being almost independent of $\log p$), $\mathrm{d}\gamma/\mathrm{d}\log p$ is also a maximum under these conditions. Inspection of the values of d, D, and A shows that as $1/(d - 0{\cdot}220)$ decreases, D/A increases, so that in fact the points of inflexion in the plots of γ against log p all occur just above or within the experimental range. Below ~10 mm. therefore, Fig. 1 shows a family of divergent curves which, within the limits of our method, do not intersect. The order of increasing association for a given series of alcohols at say 10 mm. is then identical with that given by the ultimate degrees of association. Alternatively, comparison of ultimate degrees of association is equivalent to a comparison of γ at points of maximum $\mathrm{d}\gamma/\mathrm{d}\log p$.

The circumstance that measurements have not yet been made at very low vapour pressure does not therefore invalidate the correlation of molecular structure and (ultimate) degrees of association attempted.

Correlation of Degrees of Association of Alcohols and Molecular Structure.—It seems to be generally assumed that a steric factor inhibiting association operates even for the simpler alcohols such that straight-chain alcohols would be expected to be more associated than secondary alcohols, which in turn would be more associated than tertiary alcohols. Thus it has been argued by Klyne [2] that the decrease in boiling point which occurs with increasing branching in a series of isomeric aliphatic alcohols is due in the main to a decrease in association. We find this argument unconvincing since the lowering which occurs in the boiling point of the corresponding thiols is practically identical in magnitude.

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[1] Thomas, *J.*, 1947, 822.

[2] Klyne, " Progress in Stereochemistry," Butterworths Scientific Publications, Vol. 1, 1954, 233.

Again, the difference in boiling point between, say, n-pentane and neopentane (48°) is greater than that between those of n-butyl alcohol and t-butyl alcohol (34°); indeed these figures could equally well lead to the argument that t-butyl alcohol is more associated than n-butyl alcohol. It appears to us that the high boiling point of an associated compound is due fundamentally to the high electrostatic interaction between the hydroxyl groups and that, whereas this does lead to strong association, there need not be any simple relation between boiling point and extent of association.

Our results show that in the simpler alcohols studied, a steric inhibiting factor is absent; indeed, instead of an inverse correlation between extent of branching and degree of association, we have found that branching leads to an increase in association.

Thus from the tabulated values of γ_{ult}, we conclude that:

(*a*) The lowest association occurs in methanol with the most open environment for the hydroxyl group.

(*b*) An increase in association occurs from methanol to ethanol (α-substitution), and a further but lesser increase from ethanol to propan-1-ol (β-substitution). A small decrease then occurs with further increase in chain length.

(*c*) Progressive α-substitution by methyl (or ethyl) groups into methanol causes progressive increases in γ up to 1,1-dimethylethanol and 1-ethyl-1-methylpropan-1-ol; association is then at a maximum. Study of such highly-branched compounds as say $Bu^t_3C{\cdot}OH$ would be of great interest; it might well be that a steric, inhibiting, factor would then be revealed—in other words, the limit of association may have been reached with the lower tri-n-alkylmethanols.

(*d*) Similar α-substitution into butan-1-ol and higher n-alcohols also causes increases in γ but the effect is not as marked as in the series referred to in para. (*c*). In other words, a decrease in association occurs with increase in chain length if the immediate neighbourhood of the hydroxyl group is unchanged.

(*e*) The effect of β-substitution into n-alcohols is similar but less marked.

(*f*) Substitution in γ- and δ-positions also causes a definite though smaller increase in association. Since such substitution cannot appreciably affect the environment of the hydroxyl group, the effect is probably connected with departure of the chain from linearity. This is examined further in the following paper.

(*g*) Once substitution has occurred in the α-position, subsequent substitution further along the chain does not significantly affect γ.

These observations lead to the general conclusion that association is least for straight-chain alcohols on account of the linear nature of the molecules. Conversely, association is greatest with the nearest approach to spherical shape in the immediate neighbourhood of the hydroxyl group, *i.e.*, when the substance has its centre of symmetry falling as near as possible to the hydrogen bond.

The Occurrence of a Steric Factor in the Association of Phenols.—On the basis of the magnitude of the shift in the O–H stretching frequency in the infrared absorption spectra to higher wavelength as the result of the involvement of the hydrogen atom in a hydrogen bond, Coggeshall,[3] Sears and Kitchen,[4] and Puttnam,[5] examined a number of alkylphenols. When the difference in wavelength ($\Delta\lambda$) between a dilute solution and a concentrated solution or liquid melt is considered, the phenols can be divided into (sterically) unhindered phenols substituted *meta* or *para* only, and "hindered" phenols substituted in both *ortho*-positions by large groups such as t-butyl. The effect of such substituents as *ortho*-isobutyl is intermediate, as also is the effect of only one t-butyl group. According to Sears and Kitchen, even *ortho*-methyl groups have a certain effect, although this was not the view of Coggeshall.

The previous results on phenols (Part III), supplemented by the present work on

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[3] Coggeshall, *J. Amer. Chem. Soc.*, 1947, **69**, 1620.

[4] Sears and Kitchen, *J. Amer. Chem. Soc.*, 1949, **71**, 4110.

[5] Puttnam, *J.*, 1960, 486.

3-methyl-6-t-butyl- and 2,6-di-t-butyl-phenol, would appear to support these findings. Thus, whereas the cresols (see Fig. 1b) and phenol itself are associated to approximately the same extent, 3-methyl-6-t-butylphenol (partially hindered) is associated only to the extent of ~20% at its boiling point. The degree of association of the fully-hindered 2,6-di-t-butylphenol is still further depressed (Fig. 1b).

However, the decrease in association is probably not entirely due to the proximity of the t-butyl groups, for a similar but less-marked decrease seems to result in general from substitution, even in *meta*- and *para*-positions, by groups other than methyl irrespective of the electronic nature of the group (*p*-chlorophenol, *m*- and *p*-methoxyphenols, and methyl *p*-hydroxybenzoate; cf. Part III). Again for alkylphenols, reduced acidity could be a contributory factor.

The operation of a steric factor in phenols is to be expected since the oxygen atom of the hydroxyl group and the α-carbon atom of the substituent are necessarily coplanar. A steric inhibiting factor functioning in alcohols by simply shielding the hydroxyl group is absent in the compounds studied, although it might well arise in a compound such as, say, $Bu^t_3C{\cdot}OH$.

In contrast to the behaviour of phenols, there do not appear to be any significant differences in the values of $\Delta\lambda$ between a straight-chain alcohol and its branched-chain isomer.[6,7]

EXPERIMENTAL

Vapour pressures were measured as outlined in Part III, and smoothed values, read from a a large-scale graph of log *p* against *t*, are recorded in Table 3. We have compared the results for 5 alcohols with those of Butler, Ramchandani, and Thomson [8] by evaluating temperatures corresponding to their published vapour pressures. Agreement is satisfactory, our results for a given alcohol being either consistently a fraction of a degree lower or higher than their temperatures.

TABLE 3.

Temperatures (°c) corresponding to values of $\log_{10} p$, where p is the vapour pressure (mm.).

$\log_{10} p$ ……	0·8	1·0	1·2	1·4	1·6	1·8	2·0	2·2	2·4	2·6	2·8	2·8808	2·8808 (lit. values)	
Compd. I	—	16·9	23·4	30·3	37·6	45·4	53·8	62·9	72·5	82·9	94·2	99·2	99·5 [1]	
,, II	37·3	44·6	52·1	59·8	67·9	76·4	85·5	95·7	106·6	118·6	131·8	137·9	137·9 [1] to 138·2	
,, III	24·8	31·7	38·8	46·1	53·6	61·7	70·4	79·8	90·0	101·0	113·3	119·2	119·8 [1]	119·5 [5]
,, IV	20·6	27·6	34·8	42·2	49·8	57·9	66·6	76·1	86·2	97·3	109·7	115·5	116·0 [1]	115·6 [5]
,, V	33·6	39·7	46·4	53·5	61·3	69·8	78·6	88·2	98·6	110·1	122·6	128·2	128 [1]	128·0 [2]
,, VI	—	25·3	32·0	39·1	46·7	54·8	63·5	72·7	82·8	93·8	106·1	111·4	111·5 [2]	
,, VII	49·7	57·1	64·8	73·0	81·8	91·1	101·1	111·9	124·1	137·3	151·8	158·2	158·5 [2]	158 [5]
,, VIII	52·0	59·5	65·5	73·2	81·5	90·6	100·3	111·0	123·0	136·3	150·5	156·6		
,, IX	47·4	54·9	62·7	70·8	79·3	88·5	98·2	108·8	120·5	133·4	148·0	154·2	155·4 [3]	
,, X	38·4	46·1	54·0	62·0	70·2	78·8	88·1	98·4	109·8	122·6	136·7	142·8	142·2 [5]	
,, XI	34·3	41·1	48·2	55·8	64·1	73·3	83·1	93·5	105·0	118·1	132·6	139·0	140 [5]	
,, XII	68·2	75·2	82·9	91·2	99·8	109·2	119·5	130·8	143·0	156·2	170·5	176·6	175·8 [5]	176·3 [4]
,, XIII	82·0	89·0	96·7	105·2	114·5	124·7	135·5	147·1	159·7	173·3	188·2	194·7	195·2 [1]	194·4 [1]
,, XIV	105·0	114·3	124·2	134·6	145·8	158·0	171·0	185·1	200·2	216·5	—	—		
,, XV	113·6	123·0	133·2	144·2	156·0	168·6	182·2	196·8	212·6	—	—	—		

Refs. 1, Timmermans (ref. 13). 2, " Organic Solvents " (ref. 14). 3, " Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., 1957. 4, Rodd, " Chemistry of Carbon Compounds," Elsevier Publishing Co., 1951, Vol. 1A. 5, International Critical Tables.

Viscosities were determined with an Ostwald-type U-tube viscometer (Brit. Stand. 188), the usual precautions being observed. Temperatures were measured with a series of totally immersed short-stem thermometers, calibrated and graduated in 0·1°c.

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[6] Stanford and Gordy, *J. Amer. Chem. Soc.*, 1940, **62**, 1247.

[7] Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2492.

[8] Butler, Ramchandani, and Thomson, *J.*, 1935, 280.

Even at the highest temperatures, temperature fluctations at different points in the thermostat-bath fluid did not exceed 0·1°c.

The viscometer, after being annealed at 300° for several days, was calibrated against water by using viscosities calculated from Bingham's[9] fluidity–temperature equation at eight temperatures between 12° and 95°, and the constants in the equation $\nu = Ct - c/t$ (where ν is the kinematic viscosity in centistokes and t time in sec.), evaluated by application of Campbell's "zero sum" method,[10] to give $C = 0{\cdot}00360$ and $c = 2{\cdot}32$. The mean deviation between Bingham's best values and those calculated by us was 0·2%, with a maximum deviation of 0·4%. The minimum time of flow during the measurements never fell below the quickest time involved in the calibration. Similar recalibration after repeated use of the instrument gave values of the constants virtually identical with the above. Densities were measured by using 5—10 c.c. pyknometers as described by Reilly and Rae[11] and refer to water at 4°c.

Refractive indices were measured on an Abbé refractometer generally from ~10° to ~25°; plots of refractive index against temperature were linear within the limits of error.

Materials.—All materials were fractionated in a 12 in. × 1 in. diam. column packed with Dixon 1/16 in. × 1/6 in. gauze rings, and provided with an electrically-heated jacket regulated to maintain temperature ~25° below the distillation values. The efficiency on total reflux was ~12 theoretical plates. The recommendations of Linstead, Elvidge, and Whalley[12] (including intermittent take-off) were followed in distillations, their progress being followed both thermometrically and by means of refractive-index measurements. Any variations in column-head temperatures and refractive index during final fractionation are recorded below. Unless otherwise stated, our b. p.s (by extrapolaton or interpolation) agree satisfactorily with the best literature value (see Table 3). Before distillation, all the alcohols were dried (K_2CO_3 followed by "Drierite").

Butan-2-*ol* (I). The fraction used (ex B.D.H. material) had n_D^{15} 1·3994 (lit.[13] 1·3995), $dn/d\theta$ 0·00041, d_{30} (interpolated) 0·7987 (lit.[13] 0·7990). There was also satisfactory agreement (mean deviation, 0·6 mm.) with the vapour pressures recorded by Timmermans[13] from 12·7 mm. to 79·5 mm.; agreement over the viscosities at 15° and 30° is however poor—our value at 15° being 10% higher, and at 30° 19% lower, than those recorded by Timmermans. In view of the good agreement found for viscosity values for other alcohols, this disagreement is difficult to explain.

Temp. (θ), °c	29·6	45·1	59·2	74·6	89·0
d_4^{θ}	0·7988	0·7857	0·7721	0·7567	0·7409

θ°	14·8	25·3	33·8	45·8	53·9	66·3	75·4	83·9	95·5
η (in poises × 10^3)	46·60	30·81	22·61	15·24	11·90	8·50	6·92	5·68	4·60

Pentan-1-*ol* (II). Although our sample (500 g., ex B.D.H. material) had constant b. p. and refractive index, it was impure by comparison of its physical properties with those recorded by Timmermans[13] (in parentheses), *viz.* d_4^{30} 0·8117 (0·8076), n_D^{15} 1·4138 (1·4117), η_{30} 29·5 (29·87), $dn/d\theta$ 0·00036.

θ°	29·7	45·1	59·2	74·6	89·0	103·7	123·4
d_4^{θ}	0·8116	0·8001	0·7893	0·7765	0·7641	0·7514	0·7319

θ°	24·9	41·3	53·8	70·1	83·1	99·8	114·2	120·7	129·8
η	34·41	22·10	16·25	11·40	8·77	6·46	5·13	4·64	4·08

Pentan-2-*ol* (III). This alcohol was prepared by the Grignard reaction from propyl bromide and acetaldehyde. To remove paraldehyde which forms an azeotrope with the alcohol,[13] the product was distilled with dilute sulphuric acid (100 c.c.), and acetaldehyde, formed by depolymerisation, was removed by distillation. The residue, which no longer gave a precipitate with Fehling's solution, was washed with aqueous sodium hydrogen carbonate, and then water, and finally dried. Several fractionations then gave material, b. p. over a 0·3° range, n_D^{20}

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[9] Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co. Inc., 1922.

[10] Campbell, *Phil. Mag.*, 1920, **39**, 177; 1924, **47**, 816.

[11] Reilly and Rae, "Physico-Chemical Methods," Methuen and Co. Ltd., London, 1940, Vol. 1.

[12] Linstead, Elvidge, and Whalley, "A Course in Modern Techniques of Organic Chemistry," Butterworths Scientific Publications, London, 1955, Ch. 8.

[13] Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

1·4063 ⟶ 1·4065 (25 c.c. from 99 c.c. of original alcohol). Its physical properties, apart from a slight discrepancy in b. p. (0·6°), agreed closely with those recorded by Timmermans, *viz.* d_4^{30} 0·8017 (0·8012), n_D^{15} 1·4083 (1·4084), dn/dθ = 0·00038, η_{30} 27·9 (27·8).

θ°	20·1	30·1	41·3	50·8	74·6	93·5	108·2
d_4^θ	0·8069	0·8015	0·7923	0·7836	0·7617	0·7428	0·7274

θ°	25·4	33·6	50·0	60·1	74·5	88·8	99·5	113·3
η	33·90	24·86	14·52	10·93	7·72	5·70	4·69	3·742

Pentan-3-*ol* (IV). This alcohol was prepared by the Grignard reaction from ethyl bromide and propionaldehyde; 2 fractions were obtained, (a) b. p. 108—114°, and (b) b. p. 114—114·5°. Fraction (a) was treated with dilute sulphuric acid (see above), dried, and refractionated. Material, b. p. >114°, was combined with fraction (b) and then refractionated; the final sample boiled over a 0·4° range and had n_D^{20} 1·4102 ⟶ 1·4104. Its physical properties, apart from a slight discrepancy in b. p. (0·5°) were virtually identical with those recorded by Timmermans, *viz.*, d_4^{30} 0·8117 (0·8118), n_D^{15} 1·4123 (1·4124), dn/dθ 0·00041, η_{30} 32·8 (33·1).

θ°	19·4	29·9	41·3	50·8	74·6	93·5	108·2
d_4^θ	0·8208	0·8119	0·8015	0·7928	0·7698	0·7501	0·7336

θ°	20·1	29·8	36·9	47·2	55·1	71·1	79·5	88·4	109·0
η	53·42	32·97	24·28	16·24	12·42	7·99	6·53	5·42	3·75

2-*Methylbutan*-1-*ol* (V). The final sample (ex B.D.H. "active amyl alcohol—a racemic mixture") boiled over a 0·5° range and had n_D^{15} 1·4119, dn/dθ 0·00039, d_4^{20} (extrapolated) 0·819, d_4^{25} (extrapolated) 0·815 (lit.[14] 0·8193 and 0·8152, respectively).

θ°	29·5	51·2	64·8	79·9	94·8	105·0	117·5
d_4^θ	0·8111	0·7928	0·7814	0·7687	0·7549	0·7451	0·7343

θ°	19·3	28·9	45·7	52·0	61·1	70·5	80·2	89·6	99·9	108·6	123·0
η	55·05	38·68	22·49	18·53	14·54	11·49	9·14	7·45	6·12	5·23	4·14

3-*Methylbutan*-2-*ol* (VI). Prepared from isopropyl bromide and acetone by a Grignard reaction. The alcohol had b. p. range 0·3°, n_D^{20} 1·4093 (lit.[14] 1·4095), dn/dθ 0·00042, and d_4^{20} 0·820 (lit.[14] 0·8134), d_4^{25} 0·815 (lit.[14] 0·819), both extrapolated.

θ°	29·4	51·2	64·8	79·9	94·8	105·0
d_4^θ	0·8107	0·7901	0·7778	0·7598	0·7461	0·7346

θ°	18·2	30·8	47·5	59·4	76·5	86·5	99·2	106·8
η	53·58	30·66	16·76	11·91	7·87	6·36	5·016	4·364

Heptan-2-*ol* (VII). This was similarly prepared from pentyl bromide and acetaldehyde. Fractionation and discarding of much low-boiling material gave only a low yield of alcohol of sufficient quality for our work. It distilled over a 0·7° range and had n_D^{20} 1·4210 (International Critical Tables gives 1·4213), dn/dθ 0·00039; d_4^{20} 0·820 and d_4^{30} 0·812 [both extrapolated and both agreeing well with[4] literature values (International Critical Tables and ref. 14 give 0·819 and 0·810, respectively)].

θ°	30·1	48·0	59·2	74·8	89·3	103·6	120·0	135·3	148·3
d_4^θ	0·8118	0·7978	0·7880	0·7748	0·7615	0·7485	0·7322	0·7171	0·7035

θ°	30·0	45·9	60·1	75·3	92·3	103·7	118·7	135·1	150·2
η	33·21	20·21	13·76	9·80	7·02	5·81	4·60	3·658	3·047

Heptan-3-*ol* (VIII). Fractionation of material (Kodak Ltd., Kirkby Trading Estate, Liverpool) gave a product, b. p. range 0·1°, n_D^{15} 1·4238, dn/dθ 0·00040.

θ°	33·8	43·4	62·8	80·4	92·6	105·5	132·4	143·4
d_4^θ	0·810	0·8021	0·7858	0·7674	0·7583	0·7459	0·7166	0·7080

θ°	38·4	53·9	73·5	86·5	98·4	117·1	131·3	145·1
η	29·86	16·88	10·24	7·60	6·00	4·404	3·601	3·026

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[14] Weissberger, Proskauer, Riddich, and Toops, "Organic Solvents," Interscience Publishers, New York, 1955.

Heptan-4-*ol* (IX). This was prepared by Grignard reaction between propyl bromide and butyraldehyde and had b. p. range 0·4°, d_4^{20} 0·820 (extrapolated), n_D^{20} 1·4199 (International Critical Tables give d_4^{20} 0·820, n_D^{20} 1·421 and b. p. 1·2° higher than ours), dn/dθ 0·00042.

θ°	29·9	39·8	54·8	76·0	91·5	108·3	115·2	133·1	142·9
d_4^θ	0·8114	0·8046	0·7919	0·7734	0·7591	0·7429	0·7357	0·7173	0·7067

θ°	18·0	34·8	50·0	63·8	78·9	94·5	109·5	125·6	141·3	146·3
η	57·45	28·66	17·03	11·52	8·12	5·91	4·59	3·637	2·985	2·828

2-*Methylhexan*-2-*ol* (X). Similarly prepared from butyl bromide and acetone, this alcohol had b. p. range 0·2°, d_4^{20} 0·815 (extrapolated), n_D^{15} 1·4214, n_D^{20} 1·4193, dn/dθ 0·00041 (International Critical Tables give d_4^{20} 0·816, n_D^{20} 1·4159). The refractive index was remeasured on completion of the physical measurements to check lack of dehydration. It was unchanged.

θ°	29·9	38·8	54·6	75·9	91·6	107·4	115·1
d_4^θ	0·8064	0·7980	0·7852	0·7659	0·7498	0·7342	0·7260

θ°	32·5	45·2	60·2	75·8	90·8	110·6	122·3	133·9
η	30·16	19·74	12·83	8·82	6·43	4·48	3·84	3·321

2,4-*Dimethylpentan*-3-*ol* (XI). Fractionation of B.D.H. material gave a sample, b. p. range 0·1°, d_4^{20} 0·829 (extrapolated), n_D^{20} 1·4248 $\longrightarrow$ 1·4250, dn/dθ 0·00042 (International Critical Tables give d_4^{20} 0·829, n_D^{20} 1·4226).

θ°	33·8	43·4	62·7	80·4	92·6	105·5	121·6
d_4^θ	0·8153	0·8081	0·7893	0·7716	0·7587	0·7455	0·7292

θ°	31·0	48·4	64·6	79·7	95·2	109·5	119·3	124·6	132·8
η	34·68	16·27	9·62	6·70	5·08	4·00	3·55	3·34	3·026

Heptan-1-*ol* (XII). Fractionation of B.D.H. material (200 c.c.) gave a sample (30 c.c.) of constant b. p., n_D^{25} 1·4228. Taking dn/dθ 0·0004, we have n_D^{20} 1·4248 (cf. 1·4252, ref. 8) and $n_D^{22.4}$ 1·4238 (cf. 1·4233, International Critical Tables). The density at 22° was taken from the International Critical Tables, and the coefficients of expansion from ref. 15.

θ	108·6	123·1	138·1	153·3	160·4	168·2
ν (millistokes)	10·39	8·31	6·75	5·64	5·21	4·78

Octan-1-*ol* (XIII). A sample (30 c.c.), obtained by fractionation of B.D.H. material (100 g.), had b. p. range 0·2°, n_D^{15} 1·4316 (Timmermans gives 1·4322), n_D^{25} 1·4277 (lit.[16] n_D^{25} 1·4275) dn/dθ 0·00039. There is also satisfactory agreement (mean deviation 0·4°c) with the boiling points at four different pressures from 20 mm. to 760 mm., recorded by Dorough, Glass, Gresham, Malone, and Reid.[16] The density at 0° was taken from Timmermans [13] and the coefficients of expansion from Castell-Evans.[15]

θ°	120·8	130·8	138·5	151·8	165·8	176·5	187·1
ν	9·88	8·52	7·69	6·54	5·5565	5·041	4·483

5-*Methyl*-2-*t*-*butylphenol* (XIV). Material (Kodak Ltd.; 260 c.c.) was washed with warm 15% sodium hydroxide solution (500 c.c.), and the residue (~190 c.c.) completely dissolved in aqueous sodium hydroxide (40 g. in 160 c.c. of water). Water (~20 c.c.) was then gradually added until phenol (~40 c.c.) was regenerated. The remaining solution was diluted further, acidified with concentrated hydrochloric acid, and again treated with dilute sodium hydroxide until just alkaline. (According to Stevens,[17] the presence of acid in the product causes dealkylation during distillation.) The product was washed free from alkali, dissolved in light petroleum (40 c.c.), dried over " Drierite," and fractionated at 30 mm. pressure to give product (50 c.c.), b. p. 138·9°, m. p. (corr.; cooling-curve method) 21·0°, n_D^{20} 1·5188, dn/dθ (20—40°) 0·00044.

θ°	48·4	60·0	77·8	90·2	104·0	119·0	130·6	140·8	149·9	159·4	171·3	180·6	190·4
ν	55·35	37·02	22·83	17·27	13·45	10·65	9·07	8·05	7·31	6·68	5·95	5·46	5·05

Densities were measured at two temperatures only, $d_4^{121\cdot0}$ 0·8860 and $d_4^{159\cdot0}$ 0·8529. The values of $\sqrt{d}$ at other temperatures needed to evaluate A, D, and d were calculated by assuming that

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[15] " Physico-Chemical Tables," Griffin and Co. Ltd., London, 1902, Vol. 1.

[16] Dorough, Glass, Gresham, Malone, and Reid, *J. Amer. Chem. Soc.*, 1941, **63**, 3100.

[17] Stevens, *Ind. Eng. Chem.*, 1943, **35**, 655.

$\sqrt{d}$ is a linear function of temperature; the error thus introduced is negligible since the % variation in viscosity is very much greater than the corresponding variation in $\sqrt{d}$.

2,6-*Di-t-butylphenol* (XV). Material (250 g.; Kodak Ltd.) was agitated with 40% sodium hydroxide solution (2 × 100 c.c.), and the residue was washed with warm water. It was then dissolved in light petroleum (80 c.c.), dried, and fractionated at 30 mm. The fraction of constant b. p. 145·5° was taken as pure material. This had n_D^{35} 1·5022, dn/dθ (35—40°) 0·00044, m. p. (corr., cooling curve method) 37·3° (Kolka, Napolitano, and Ecke [18] give m. p. 36·5°). Densities were measured at two temperatures only; $d_4^{121\cdot0}$ 0·8626 and $d_4^{159\cdot0}$ 0·8291; values at other temperatures were calculated as before.

θ° ...	43·5	60·1	74·7	90·7	103·8	120·6	129·0	140·1	149·9	159·1	171·1	180·5	190·4
η ...	58·6	35·00	24·86	18·24	14·79	11·75	10·60	9·36	8·29	7·77	6·98	6·46	5·97

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[18] Kolka, Napolitano and Ecke, *J. Org. Chem.*, 1956, **21**, 712.