value, 4.4 kcal, agrees well with the values obtained, e.g., by infrared spectroscopy (*5*).

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Viscosity Behavior of Associated Liquids at Lower Temperatures and Vapor Pressures

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Kinematic viscosity measurements on 13 monohydric alcohols to a lower limit of ca. −50 °C and on six dihydric alcohols to ca. −10 °C are reported. Numerical analysis of the variation of viscosity (η) with absolute temperature (T) shows that whereas at first rapid increases in $d \log \eta v^{1/2}/d(1/T)^{\theta}$ (in which v is the specific volume and θ a constant) occur at lower temperatures the plots of $\log \eta v^{1/2}$ vs. $1/T^{\theta}$ become linear, thereby simulating under these latter conditions the behavior of nonassociated liquids. Using the vapor pressures of the preceding paper, we fitted the results to a three-constant equation expressing the variation of viscosity with vapor pressure.

Association in hydroxy compounds is most usually regarded as a stepwise process involving "chain" polymers, i.e., $A_n + A \rightarrow A_{n+1}$. On this assumption it follows that, in principle, degrees of association will increase with falling temperature and that—unless the freezing-point intervenes—the viscosity will soon reach very high values with formation of glassy solids. Due to the paucity of viscosity measurements below room temperature, this possibility has not hitherto been investigated.

Experimental Section

Materials. The samples of butan-2-ol and three pentyl and three heptyl alcohols, were those used previously (*14*); they were redistilled before use and their physical properties were unchanged. Their refractive indices at 20 °C agree with those selected by Wilhoit and Zwolinski (*18*) to on average 0.0002, and their boiling points agree to on average of 0.3 °C. For five of these compounds similar comparison is also possible for the densities at 20 °C; with the exception of pentan-2-ol for which there is a discrepancy of 0.0023 g cm^{-3}, agreement is again good—with an average difference of 0.0005 g cm^{-3}. It may also be added that the vapor pressures of all seven compounds (*14*) have been used—with other data—by Wilhoit and Zwolinski (*18*) for evaluation of Antoine vapor pressure constants.

The physical properties of five (of the six) dihydric alcohol samples have also been previously recorded (*15*). In general, dihydric alcohols have not been as extensively studied as have the lower monohydric alcohols, but when comparisons can be made, agreement is again satisfactory; thus for propan-1,2-diol, propan-1,3-diol, and 2-methylpentan-2,4-diol, refractive indices at 20 °C agree with literature values to an average 0.0003.

The six hexanols studied in the present work (Koch-Light Laboratories, Ltd., or Ralph N. Emanuel, Ltd.) were purified in the manner indicated in the preceding paper in this issue, and variations in column-head temperatures did not exceed 0.2 °C except for 2,3-dimethylbutan-2-ol which distilled over a 1 °C range and which appeared to be somewhat impure. Their refractive indices at 20 °C or 25 °C, recorded below, agree satisfactorily with those of Wilhoit and Zwolinski. A good-quality commercial ethylene glycol was similarly purified to give a material of constant boiling point and refractive index.

Viscosities. Measurements were conducted in a "Minus Seventy" thermostat bath (Townson and Mercer, Ltd.) kept to well within ±0.1 °C. Above 0 °C, temperatures were measured with a series of totally immersed NPL calibrated short-stem thermometers graduated in 0.1 °C, and below 0 °C temperatures were measured with a similarly immersed alcohol-in-glass thermometer calibrated as described in the preceding paper. Above 0 °C, temperatures were considered accurate to ±0.05 °C; below 0 °C, uncertainties in thermometry were greater, but errors exceeding 0.3 °C were thought unlikely. Kinematic viscosities (ν) were determined by using a series of "shortened-form suspended level" viscometers (British Standard 188:1957), size numbers 2 to 6 inclusive, and the equation $\nu = Ct - (c/t)$ in which C and c are constants and t is the time of flow. The values of c were those recommended in the specification. In order to exclude atmospheric moisture, the side arms of the viscometers were fitted with ground-glass cones to accommodate socketed guard tubes (*13*).

The viscometer of lowest capillary diameter was calibrated against water between 12 and 95 °C in the manner previously described (*14*) and then used to determine the viscosity of a sample of carefully purified butan-2-ol. The butan-2-ol in turn was utilized to calibrate the wider capillary viscometers used in the lower temperature measurements.

Such calibration procedure was repeated at regular intervals throughout the work in order to allow for any changes in capillary dimensions (there were in fact none). In all cases, times of flow during measurements never fell below the quickest time involved in calibration. Our results are recorded in Table I. They are considered to be accurate to within ca. 0.5% when measured above 0 °C; below this temperature, however, the average error is thought to be ca. 1.5% with the possibility that some of the individual measurements may be subject to errors up to, but not exceeding, 3%.

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Table I. Kinematic Viscosities (ν)

Butan-2-ol									
temp, °C	10.0	−0.1	−10.0	−20.0	−30.1	−40.2	−50.5		
ν, mSt	71.4	111.3	175.4	291.2	500.3	915.8	1803		
Pentan-2-ol									
temp, °C	9.3	−0.5	−10.0	−15.0	−20.6	−30.2	−40.3	−50.0	
ν, mSt	80.7	129.4	207.8	274.6	382.2	706.4	1337	2876	
Pentan-3-ol									
temp, °C	9.7	−0.6	−10.5	−21.6	−30.0	−39.0	−48.0		
ν, mSt	129.2	255.5	542.9	1417	3054	7377	20160		
2-Methylbutan-1-ol									
temp, °C	9.6	0.0	−10.0	−20.1	−30.1	−40.2	−50.5	−60.6	
ν, mSt	99.2	146.8	229.0	372.0	633.9	1132	2269	5062	
Hexan-3-ol (The final sample had $\mu^{20}{}_{\mathrm{D}}$ 1.4153–1.4158 (lit.[18] 1.4160).)									
temp, °C	0.0	−10.0	−20.2	−30.1	−40.1				
ν, mSt	256.9	557.6	1244	3542	10530				
2-Methylpentan-1-ol (The final sample had $\mu^{20}{}_{\mathrm{D}}$ 1.4180 (lit.[18] 1.4190).)									
temp, °C	9.8	−0.6	−10.4	−19.9	−30.1	−40.0	−50.2	−60.0	
ν, mSt	117.9	180.0	301.9	501.2	952.4	1851	4198	10412	
3-Methylpentan-2-ol (had $\mu^{25}{}_{\mathrm{D}}$ 1.4172 (lit.[18] 1.4179))									
temp, °C	−3.4	−12.0	−20.0	−29.8	−39.5				
ν, mSt	283.2	545.8	1178	3207	9508				
4-Methylpentan-2-ol (This material had $\mu^{20}{}_{\mathrm{D}}$ 1.4114 (lit.[18] 1.4112).)									
temp, °C	0.0	−10.0	−20.2	−30.1	−40.1	−51.0			
ν, mSt	170.4	309.3	629.4	1341	3200	9601			
2-Ethylbutan-1-ol (The final fraction had $\mu^{25}{}_{\mathrm{D}}$ 1.4200 (lit.[18] 1.4205).)									
temp, °C	−10.5	−21.6	−29.9	−39.0	−48.0				
ν, mSt	528.8	850.7	1523	3013	6651				
2,3-Dimethylbutan-2-ol (The final fraction had $\mu^{20}{}_{\mathrm{D}}$ 1.4170 (lit.[18] 1.4173).)									
temp, °C	10.0	−0.6	−10.4	−19.8					
ν, mSt	112.5	213.3	421.7	859.2					
Heptan-3-ol									
temp, °C	28.1	18.3	−0.1	−5.1	−10.2	−15.0	−25.5	−30.5	−40.0
ν, mSt	54.1	86.8	267.9	384.0	574.4	869.1	2278	3861	11200
Heptan-4-ol									
temp, °C	10.4	−1.1	−10.1	−18.6	−25.3	−35.2			
ν, mSt	139.6	303.0	651.9	1151	2370	7435			
2,4-Dimethylpentan-3-ol									
temp, °C	10.2	0.5	−6.4	−10.1					
ν, mSt	157.5	360.9	693.4	1010					
Ethan-1,2-diol[a] (had $\mu^{20}{}_{\mathrm{D}}$ 1.4312 (lit.[17] 1.4318))									
temp, °C	167.6	159.9	149.6	140.7	131.1	119.6	110.1		
ν, mSt	7.63	8.31	9.40	10.53	12.06	14.26	16.45		
temp, °C	101.8	83.3	74.2	63.8	56.2	34.8	25.1	17.1	8.1
ν, mSt	19.23	26.61	33.40	42.9	52.6	104.7	151.3	215.8	334.1
Propan-1,2-diol									
temp, °C	64.9	49.9	35.0	20.4	9.4	0.3	−10.4		
ν, mSt	71.6	128.9	257.2	581.3	1155	2332	5603		
Propan-1,3-diol									
temp, °C	64.9	49.9	35.0	20.4	9.5	0.3	−10.4	−20.4	−32.0
ν, mSt	91.2	149.1	263.8	500.6	841	1413	2952	6176	16980
Butan-1,4-diol									
temp, °C	83.3	70.4	55.1	39.4	30.3	18.2			
ν, mSt	79.4	117.8	198.4	366.6	546.6	983			
3-Methylpentan-1,5-diol									
temp, °C	93.4	53.7	37.0	18.0	7.9	0.5	−11.0		
ν, mSt	80.5	331.7	723.5	1916	3616	6039	14760		
2-Methylpentan-2,4-diol									
temp, °C	53.7	37.0	25.5	15.5	0.1	−9.9			
ν, mSt	75.5	153.2	278.9	562.3	1932	4957			

[a] Our (interpolated) calculated values of η at 15 and 30 °C (261 and 137 mP, respectively) agree satisfactorily with those of Timmermans (*17*) (261 and 133.5 mP). Our values are, however, uniformly higher by 3–4% than those reported by Ražnjević (*6*), between 20 and 140 °C.

Except for the six hexanols and ethylene glycol, we have previously recorded (*14*, *15*) the viscosities, at room temperature and upward, of all the materials considered in the present work; the present values therefore serve to extend the previous data to lower temperatures. Although repeat measurements at overlap temperatures have not been conducted, numerical

Table II. Parameters of Equation 3 and Derived Values of d log $\eta v^{1/2}$/d log p[a]

compound	temp range, °C	% dev of eq 3	constants of eq 3 A	constants of eq 3 D	constants of eq 3 d	d via (Δ log $\eta v^{1/2}$)/$(1/T)^\theta$	lit. density data	lit. vapor pressure
butan-2-ol	−10 to 96	1.0	6	158.5	0.58	0.53	14	14
pentan-2-ol	−30 to 113	1.1	8	94.2	0.57	0.54	14	14
pentan-3-ol	−30 to 109	2.2	14	216.3	0.82	0.77	14	14
2-methylbutan-1-ol	−20 to 123	1.3	4	87.1	0.483	0.50	14	14
hexan-3-ol	−20 to 125	2.4	11	105.4	0.70	0.76	4	4, 15
2-methylpentan-1-ol	−10 to 135	1.5	4	64.9	0.47	0.48	4	4, 15
3-methylpentan-2-ol	−20 to 125	2.8	14	90.2	0.72	0.79	2	2, 15
4-methylpentan-2-ol	−20 to 125	2.8	7	92.9	0.577	0.64	4	4, 15
2-ethylbutan-1-ol						0.55	3	
2,3-dimethylbutan-2-ol						0.74	2	
heptan-3-ol	−10 to 145	3.4	12	47.1	0.66	0.70	14	14
heptan-4-ol						0.70	14	
2,4-dimethylpentan-3-ol						0.95	14	
ethan-1,2-diol	56 to 168	0.8	12	42.5	0.41	0.41	6, 17	7
propan-1,2-diol						0.64	5, 15	
propan-1,3-diol						0.46	5, 15	
butan-1,4-diol						0.43	15	
3-methylpentan-1,5-diol						0.46	15	
2-methylpentan-2,4-diol						0.71	7, 15	

[a] Viscosity in mP, vapor pressure in torr, and specific volume in cm^3 g^{-1}.

differentiation (see below) showed that in no case was there any discontinuity between our two sets of data. For the hexanols, our lower temperature values supplement those of Hovorka et al. (*2–4*) which were made at room temperature to respective boiling points, but it is only for 2-ethylbutan-1-ol that the two sets of data fail to "marry".

Results and Discussion

Analysis of Viscosity vs. Temperature Behavior. L.H.T. has shown (*11*) that below a few atmospheres pressure, the vapor pressure (p) of nonassociated liquids is accurately reproduced by the equation

$$\log p = \log \psi - (I/T^\theta) \qquad (1)$$

in which ψ is a universal constant (=1.9 × 10^6 when pressure is expressed in torr), I and θ are specific constants, and T is temperature, Kelvin scale. In the preceding paper it was demonstrated that the equation is also applicable to associated liquids in the range ca. 0.1–760 torr.

The author has also shown (*12*) that for nonassociated liquids, the variation of viscosity with temperature is given by the relationship

$$\log \eta v^{1/2} = \alpha + (aI/T^\theta) \qquad (2)$$

in which v is the specific volume and α is a constant for a given substance. The constant a (=d log $\eta v^{1/2}$/d log p from eq 1) is the ratio of the energy of activation of viscous flow to the energy of vaporization (*10*, *12*), which for all but a very few highly symmetrical molecules has sensibly the same numerical value (0.220) for all nonassociated substances.

To utilize the data of the present work, kinematic viscosities (ηv) were converted into $\eta v^{1/2}$ values by using the density vs. temperature data of Thomas and Meatyard (*14*, *15*) and Hovorka et al. (*2–4*), supplemented by data—mostly at room temperature only—taken from Pollock and Stevens (*5*), Timmermans (*17*), Ražnjević (*6*), or Shell Chemical Corp. (*7*). Further details are given in Table II. In most cases, it was necessary to extrapolate the density data to lower temperatures—a procedure undertaken by assuming with Albertosi (*1*) that $(1/v)^{5/3}$ is a linear function of temperature. Bearing in mind that an increase in viscosity of about 5000 times occurs with a corresponding decrease in $v^{1/2}$ of only ca. 1.1 times, we feel any error in this procedure is quite negligible in the context of the calculations of the present paper.

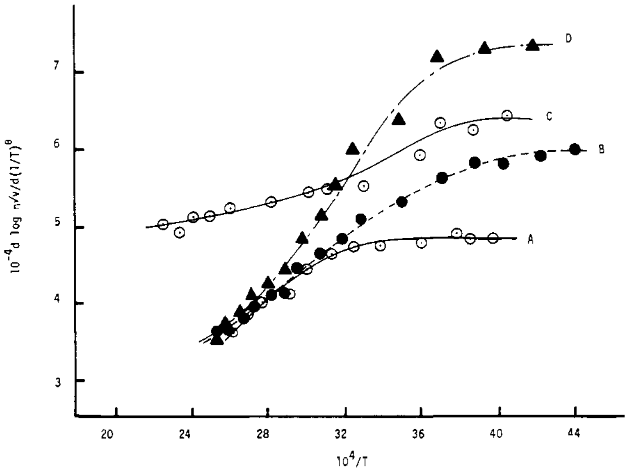

Figure 1. Plots of the differential d log $\eta v^{1/2}$/d$(1/T)^\theta$ against reciprocal of absolute temperature: (A) pentan-2-ol, (B) 4-methylpentan-2-ol, (C) propan-1,3-diol, (D) hexan-3-ol.

With the exception of n-alcohols (thus, e.g., the results of Hovorka et al. (*4*) for hexan-1-ol between 5 and 155 °C gave a = 0.37 and a mean deviation between experimental and calculated values of $\eta v^{1/2}$ of 0.9%), eq 2 does not generally hold for associated compounds at around room temperatures.

Using, however, the θ values of the preceding paper, we may calculate d log $\eta v^{1/2}$/d$(1/T^\theta)$ by numerical differentiation, and then plot against, say, $1/T$. In this way it is found that whereas at first rapid increases in the values of the differential occur, they become demonstrably constant at lower temperatures. Such plots—taking θ = 1.7 for convenience of reproduction (see previous paper)—are shown in a number of cases in Figure 1.

Differentiation of eq 2 shows that these limiting values equal dI, in which d is a constant >0.220. Such values of d (I is evaluated from vapor pressure data and eq 1) are shown in Table II.

Analysis of Viscosity vs. Vapor Pressure Behavior. An equation relating the viscosity of associated liquids with vapor pressure—which does not, like eq 2, suffer from a limited range of applicability—has previously been proposed (*8*), viz.

$$\eta v^{1/2} = (A/p^{0.220}) + (D/p^d) \qquad (3)$$

in which A and D are constants and d has the same significance as above. At sufficiently low vapor pressure, $D/p^d \gg A/p^{0.220}$ thereby giving directly ultimate constant values of d log $\eta v^{1/2}$/d

Table III. Comparison between Experimental and Calculated Values of $\eta\nu^{1/2}$ and d log $\eta\nu^{1/2}$/d log p for Pentan-3-ol[a]

			d log $\eta\nu^{1/2}$/d log p		$\eta\nu^{1/2}$		
t, °C	log p	mean log p	exptl	calcd from (3)	exptl	calcd from (3)	% dev
109.0	2.788	2.616	0.44	0.40	4.38	4.52	+3.3
88.4	2.443	2.355	0.45	0.45	6.23	6.20	−0.6
79.5	2.267	2.181	0.49	0.48	7.47	7.43	−0.1
71.1	2.094	1.913	0.52	0.53	9.10	9.00	−1.1
55.1	1.732	1.632	0.57	0.59	13.98	14.05	+0.5
47.2	1.532	1.394	0.62	0.63	18.20	18.43	+1.3
36.9	1.257	1.159	0.67	0.68	27.05	27.55	+1.8
29.8	1.061	0.920	0.73	0.71	36.59	37.40	+2.2
20.1	0.779	0.597	0.82	0.74	58.99	59.00	+0.0
9.7	0.415	0.217	0.76	0.77	117.9	110.3	−6.4
−0.6	0.020	−0.190	0.79	0.79	234.4	222.0	−5.3
−10.5	−0.400	−0.667	0.78	0.81	501.4	478.0	−4.6
−21.6	−0.935	−1.149	0.78	0.81	1318	1287	−2.3
−30.0	−1.363				2855	2860	+0.0

[a] Viscosity in mP and vapor pressure in torr.

log p = d. At the time, low vapor pressure data were not available and attainment of such constant values was merely implied. Using, however, the lower temperature viscosity and vapor pressure data reported in this and the preceding paper (*16*), respectively, we have demonstrated that such constant values have now been attained.

Solving eq 3 in the manner previously explained (*8*) and using the viscosity data specified above, we obtained the values of A, D, and d (taking η in millipoise, p in torr, and v in cm^3 g^{-1}) as shown in Table II. Mean percent differences between experimental and calculated values of $\eta v^{1/2}$ and literature sources of vapor pressure are also given.

By way of example, Table III compares individual experimental and calculated values of $\eta v^{1/2}$ in the case of pentan-3-ol. Ultimate attainment of linear log $\eta v^{1/2}$ vs. log p behavior is demonstrated by (a) numerical differentiation and (b) differentiation with eq 3.

The ten compound overall mean deviation between experimental and calculated values of $\eta v^{1/2}$ is 1.9%. If we bear in mind (a) that there are experimental difficulties involved and (b) that very great changes in both viscosity and vapor pressure occur (e.g., for pentan-3-ol, $\eta v^{1/2}$ increases 65-fold, with a corresponding change in vapor pressure of 14 000-fold), agreement is satisfactory and further testifies to the reliability of our measurements. Furthermore, the nature of the individual deviations (e.g., Table III) are such that no systematic departure from that defined by eq 3 is apparent.

The ten values of d (Table II) obtained directly from eq 3 are seen to be in satisfactory agreement with the values derived from analysis of viscosity vs. temperature behavior.

We may conclude therefore that, in general, monohydric and dihydric alcohols exhibit linear plots of log $\eta v^{1/2}$ against both $1/T^{\theta}$ and log p under appropriate conditions, thereby simulating—but with much higher energies of activation—the behavior of nonassociated compounds. Whereas n-alcohols behave in this way at room temperature, other monohydric and also dihydric alcohols do so only at temperatures lower than previously studied.

We believe that such behavior is not consistent with the usual chain-polymer model but can reasonably be claimed to favor the "ring" polymer hypothesis (*9*) and the view that at sufficiently low temperatures hydroxy compounds attain constant limiting degrees of association.

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