

Vapor Pressures and Molar Entropies of Vaporization of Monohydric Alcohols

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Vapor pressures of nine alcohols in the range 0.04 to about 3 torr have been measured. The results, together with literature data in a higher vapor pressure range, have been fitted to a three-constant (one of which is universal) equation previously developed in these laboratories for nonassociated liquids. The equation readily permits evaluation of latent heats of vaporization, and, for *n*-alcohols, H-bond enthalpies are simply related to the parameters of the equation.

Reliable determination of vapor pressure below ca. 10 torr is well-known to involve special problems (10) and, with few exceptions (12), published values in this region are inherently prone to systematic error (13). For alcohols, it appears that the only reliable data are those of Mündel (4) for methyl, ethyl, and *n*-propyl alcohols below 1 torr and possibly those of Drucker et al. (2) below 0.4 torr for ethyl alcohol.

The present work was undertaken partly to make good this deficiency but mainly to provide data in connection with continuing work on molecular association of hydroxy and other compounds in the pure, liquid state.

Experimental Section

Materials. With the exception of the five hexanols, the materials were those used previously (9); they were redistilled before use and their physical properties were unchanged. The five hexanols (Koch-Light Laboratories, Ltd., or Ralph N. Emanuel, Ltd.) were dried and fractionated in the manner described in earlier work (9). Variation in column-head temperatures did not exceed 0.2 °C. The physical properties of the materials are recorded in the following paper of this issue along with assessment of purity.

Vapor Pressure. Vapor pressures are measured by a modified Ramsay and Young method in the manner outlined in previous work (10), keeping the cooling coil at ca. -50 °C by circulation of isopropyl alcohol from a reservoir held at -70 °C. Below 0 °C, a works-certificated alcohol-in-glass thermometer was employed. It was calibrated in situ (a) under atmospheric conditions against the boiling points of CHCl₂F, CCl₂F₂, and CHClF₂ (Arcton Refrigerants, Imperial Chemical Industries, Ltd.) and propane (Air Products, Ltd.) and (b) against the boiling temperatures of pure ether under reduced pressure by using the best literature vapor pressure data available (12). Methods (a) and (b) agreed well within the limits of experimental error.

All temperature readings were taken with a rising meniscus. Above 0 °C uncertainties in thermometry as such were considered not to exceed 0.1 °C and below 0 °C about 0.3 °C.

Results and Discussion

The experimental results are given in Table I, and limits of error involved in the method have been considered previously (10, 11). It is considered that the boiling temperatures at their recorded vapor pressures are on average accurate to within ±0.2 °C at vapor pressures above 0.5 torr and to within ±0.3 °C from 0.5 to 0.1 torr. Below 0.1 torr, experimental error

Table I. Vapor Pressures (in Torr) for Nine Monohydric Alcohols

	Pentan-2-ol					
temp ^a	-32.0	-28.8	-23.6	-17.5	-13.3	-8.2
pressure ^b	0.026	0.041	0.071	0.135	0.225	0.39
temp	-3.2	0.7	5.3	9.4	13.5	18.2
pressure	0.63	0.86	1.35	1.85	2.7	3.85
temp	21.9					
pressure	5.2					
	Pentan-3-ol					
temp	-28.1	-23.4	-18.9	-15.1	-10.4	-5.8
pressure	0.054	0.095	0.15	0.25	0.40	0.63
temp	5.9	10.2	17.1	20.6		
pressure	1.9	2.65	4.7	6.05		
	2-Methylbutan-1-ol					
temp	-24.2	-21.6	-15.2	-11.4	-2.7	4.4
pressure	0.038	0.051	0.10	0.15	0.38	0.66
temp	11.4	17.5	21.7	30.0	36.1	
pressure	1.25	2.0	3.0	5.0	8.0	
	Hexan-3-ol					
temp	-19.2	-13.3	-7.8	-1.8	3.5	9.3
pressure	0.042	0.080	0.15	0.27	0.44	0.78
temp	13.1	17.7	21.6			
pressure	1.15	1.7	2.3			
	2-Methylpentan-1-ol					
temp	-11.8	-9.0	-6.9	-3.8	-0.5	4.9
pressure	0.035	0.056	0.069	0.094	0.14	0.23
temp	7.9	12.0	17.0	20.9		
pressure	0.32	0.48	0.72	1.1		
	3-Methylpentan-2-ol					
temp	-18.1	-15.5	-12.1	-8.8	-5.6	-2.1
pressure	0.046	0.063	0.095	0.14	0.195	0.28
temp	4.9	10.2	15.0	18.7	21.3	
pressure	0.53	0.87	1.45	1.9	2.2	
	4-Methylpentan-2-ol					
temp	-23.3	-19.3	-16.5	-13.6	-10.7	-6.6
pressure	0.030	0.055	0.070	0.097	0.14	0.205
temp	-2.4	2.7	6.3	9.9	13.6	17.5
pressure	0.33	0.54	0.73	1.05	1.4	2.0
temp	21.8					
pressure	2.8					
	2-Ethylbutan-1-ol					
temp	-10.4	-7.4	-2.6	1.0	5.4	10.1
pressure	0.043	0.058	0.090	0.15	0.225	0.38
temp	14.9	18.5	21.9			
pressure	0.56	0.80	1.1			
	Heptan-3-ol					
temp	-9.5	-8.0	-4.4	1.4	6.0	9.4
pressure	0.033	0.041	0.058	0.11	0.16	0.25
temp	13.8	18.0	21.5			
pressure	0.37	0.55	0.74			

^a In °C. ^b In torr.

progressively increases with loss of precision of the pressure-reading instrument (Vacustat, Edwards and Co., Ltd.), but even at such low vapor pressures, errors in individual values are unlikely to exceed about 0.5 °C.

The results reported, therefore, while (bearing in mind the difficulties inherent in measurements at such pressures) of no great precision, are confidently regarded as free from systematic error.

Table II. Constants of Equation 1 and Mean Deviations between Experimental and Calculated Boiling Temperatures (p and ψ in Torr)

compound	exptl range torr ^a	constants of eq 1		deviations (in °C)		lit.
		θ	I	mean	max	
pentan-2-ol	0.071	1.7232	100 366	0.3	1.0	9
pentan-3-ol	0.054	1.7328	104 035	0.2	0.7	9
3-methylpentan-2-ol	0.063	1.7319	111 878	0.3	0.9	9
2-methylbutan-1-ol	0.10	1.7320	110 009	0.6	1.1	9
heptan-3-ol	0.11	1.6924	96 829	0.5	1.0	9
2-methylpentan-1-ol	0.094	1.7026	99 810	0.3	0.6	3
2-ethylbutan-1-ol	0.090	1.7448	127 256	0.7	1.6	3
hexan-3-ol	0.080	1.7198	104 582	0.6	1.5	3
4-methylpentan-2-ol	0.097	1.7180	101 924	0.6	1.9	3
ethanol	23.4	1.7013	73 013	0.3	0.6	12
propan-1-ol	14.5	1.7490	105 865	0.4	0.7	12
butan-1-ol	9.57	1.7473	114 964	0.1	0.2	1
pentan-1-ol	26.01	1.7149	103 055	0.1	0.3	1
hexan-1-ol	9.75	1.7378	128 248	0.1	0.2	1
heptan-1-ol	14.35	1.7201	123 741	0.2	0.4	1
butan-2-ol	10.00	1.7650	117 238	0.1	0.2	9
3-methylbutan-2-ol	15.85	1.7415	107 776	0.1	0.3	9

^a Tabulated values to atmospheric.

Table III. Comparison of Experimental and Calculated Boiling Temperatures (in °C) for Pentan-3-ol

vapor pressure, torr	boiling temp, °C			vapor pressure, torr	boiling temp, °C		
	exptl	calcd	dev		exptl	calcd	dev
0.054	-28.1	-28.3	-0.2	6.05	20.6	20.9	+0.3
0.095	-23.4	-23.5	-0.1	15.85	34.8	34.5	-0.3
0.15	-18.9	-19.6	-0.7	39.8	49.8	49.5	-0.3
0.25	-15.1	-14.9	+0.2	63.1	57.9	57.7	-0.2
0.40	-10.4	-10.4	±0.0	100.0	66.6	66.5	-0.1
0.63	-5.8	-5.7	+0.1	158.5	76.1	76.0	-0.1
1.9	5.9	6.4	+0.5	251.2	86.2	86.3	+0.1
2.65	10.2	10.3	+0.1	398.1	97.3	97.5	+0.2
4.7	17.1	17.5	+0.4	631.0	109.7	109.6	-0.1

L.H.T. has recently shown (θ) that below a few atmospheres pressure, the vapor pressure (p) behavior of nonassociated liquids is accurately reproduced by the equation

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

in which ψ is a universal constant ($= 1.9 \times 10^6$) when pressure is expressed in torr, I and θ are specific constants, and T is temperature, Kelvin scale.

That the equation is also applicable to associated liquids is now demonstrated in Tables II and III, values of θ and I being calculated in the usual way by a least-mean-squares fit. The first part of Table II uses the data of the present paper in the more "difficult" range ca. 0.1–10 torr supplemented by our previous results (9) to atmospheric pressure. Mean and maximum deviations are shown in columns 3 and 4, respectively. The overall average mean deviation is 0.3 °C, and there is no indication of any systematic departure from linear $\log p$ vs. I/T^θ behavior.

By way of example, Table III compares experimental and calculated boiling temperatures in the case of pentan-3-ol.

The calculations forming the second part of Table II are based on our data in the lower region supplemented above ca. 30 torr by those of Hovorka et al. (3). For 2-methylpentan-1-ol, the mean deviation is satisfactory; for the three remaining compounds, however, the two sets of data do not "marry" well in the overlap region 3 to (say) 15 torr, and deviations are higher than usual. Whether this is due to experimental error or use of samples of differing purity is difficult to ascertain. Omitting

the data of Hovorka et al. and using the data of Table I at ca. 0.1 torr and above, we find the mean deviations are 0.0 °C, 0.1 °C, 0.0 °C, and 0.1 °C, respectively, but now of course the experimental ranges are more restricted (37 °C on average).

For comparative purposes, the third part of the Table II utilizes the reliable data of Butler et al. (7) and those selected by Timmermans (12)—both in the "easier" range ca. 10 torr to atmospheric—together with data in the same range from our laboratories for the two secondary alcohols (9). Comparison of these with the data for the first and second sections of Table II shows that in spite of the greater experimental ranges involved in the latter, the mean deviations do not differ appreciably. This would appear to support our contention that the data of the present paper can be accepted with some confidence as free from systematic error.

A noteworthy feature of the listed θ values is that they do not increase with molecular weight in the manner characteristic of nonassociated homologous series. An overall value, $\theta = 1.7$, could probably be used in eq 1 with little loss of accuracy.

Latent Heats and Entropies of Vaporization and H-bond Enthalpies

Below about 100 torr, vapors behave ideally and application of the thermodynamic relationship $L = RT^2 d \ln p/dT$ to (1) gives

$$(L/T) = \Delta S = R\theta \ln(\psi/p) \quad (2)$$

in which L and ΔS are the molar heats and molar entropies of vaporization, respectively. Insertion of numerical values, and expressing ΔS in calories per mole per degree, gives $\Delta S = 19.57\theta$ at 100 torr and $\Delta S = 15.53\theta$ at atmospheric pressure. In the latter case, however, it must be remembered that at atmospheric pressure vapors do not strictly behave ideally.

It may be of interest to add that for those alcohols which have attained constant degrees of association (see following paper), the enthalpy of H bonding (H) on the "ring" polymer model is readily shown to be given by the relationship

$$H = T_{100}\{(\Delta S)_{100} - (\Delta S)'\}$$

in which $(\Delta S)'$ is the molar entropy the substance would possess in the hypothetical event of its being nonassociated at the vapor pressure (100 torr) of the real substance (θ). Values so determined—after conversion to the more usual "chain" polymer model (7)—are 4.8, 4.4, 4.5, 3.9, 4.4, and 4.5 kcal, respectively, for the six n -alcohols from ethyl to heptyl inclusive. The mean

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 $\pm 0.1^{\circ}\text{C}$. 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 $\pm 0.05^{\circ}\text{C}$; 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%.