

484. *Solutions of Alcohols in Non-polar Solvents. Part V.* Values at 0° C of the Coefficients of Expansion, the Isothermal Compressibility, and the Quantity $(\partial S/\partial V)_T$ for the Normal Primary Alcohols from Methanol to Octanol.*

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Measurements have been made at 0° C of the coefficient of expansion α and the isothermal compressibility β of the first eight normal primary alcohols. The derived values of $(\partial S/\partial V)_T = \alpha/\beta$, which have a probable error of $\sim \pm 0.6\%$, do not show any simple dependence on the number of carbon atoms in the alcohol molecule. A relatively large increase in $(\partial S/\partial V)_T$ from ethanol to propanol is followed by a decrease for the next two stages of the ascent of the series, but from pentanol onwards there is an increase. Since $(\partial S/\partial V)_T$ is a measure of the rate at which the entropy increases when the molecules of the liquid are separated isothermally, it should be greater the more ordered the liquid and the more disorder it has to gain on expansion. It therefore seems that the relative degree of order in the normal primary alcohols is not a simple function of the length of the hydrocarbon chain.

PREVIOUS Parts have shown that some properties of dilute solutions of primary alcohols and glycols in non-polar solvents do not alter smoothly with increasing chain length of the solute molecules. There is sometimes evidence of alternation effects from one alcohol to the next, and sometimes changes in the solute-solvent relation when a certain chain length is reached. It is therefore pertinent to ask how, for the pure primary liquid alcohols, properties related to the intermolecular order alter with increasing chain length. An obvious property to examine is the entropy of vaporization, compared for different alcohols on the basis of the Hildebrand rule. Since any structural peculiarities will be more marked the lower the temperature, it is desirable to make this comparison at low rather than high temperatures. However, when the vapour pressure of a liquid is small, it is not easy to determine the heat of vaporization precisely enough either directly by calorimetry or indirectly from vapour-pressure measurements. We have therefore measured instead the quantity $(\partial S/\partial V)_T$. This measures, in effect, the rate at which the entropy of the system increases as the molecules are separated isothermally. The more ordered a liquid, the more disorder it has to gain on separating its molecules. It is reasonable to suppose that this will be reflected in the value of $(\partial S/\partial V)_T$. This quantity has the great advantage of being accurately measurable however involatile the liquid, since it is identically equal to α/β , where α is the coefficient of expansion and β is the isothermal compressibility. $(\partial S/\partial V)_T$ is also equal to $(\partial p/\partial T)_V$, the product of which with T is the so-called internal pressure which in the hands of Hildebrand and others has played such a large part in solution theory. Measurement of α and β is in fact one of the best methods of determining the internal pressure, but as Hildebrand and Scott have pointed out,¹ it has not been used as much as it might since values of α in the literature are sometimes ambiguously expressed and values of β are often mean values over a pressure range. The values of α and β now presented are the true thermodynamic values for each alcohol under a pressure of one atmosphere.

As a compromise between experimental convenience, the preference for a low temperature (which favours greater order within the liquid), and the need to compare as many alcohols as possible (after propanol, their m. p.s rise continuously), we have made measurements at 0° on the first eight normal primary alcohols.

* Part IV, Staveley and Milward, *J.*, 1957, 4369.

¹ Hildebrand and Scott, "Solubility of Non-electrolytes," Reinhold Publishing Corporation, New York, 1950, p. 427.

EXPERIMENTAL

The isothermal compressibility of each alcohol at 0° was determined by applying pressures up to 45 atm. and measuring the change in volume. The piezometer used (Fig. 1) had walls 6 mm. thick and a capacity of *ca.* 30 ml. The emergent capillary was in two parts. The upper part, ending in an A7 cone, was *ca.* 3 mm. i.d. to allow for expansion. The rest of the capillary was *ca.* 1 mm. i.d., and had been accurately calibrated over a length of 18 cm. adjacent to the wider capillary. This portion also had etched reference marks. In Fig. 1 the piezometer is shown attached to the fitting used to join it to the metal line leading to the source of pressure (a nitrogen cylinder) and the pressure gauges. This fitting simplified removal and replacement of the piezometer. There is a slight bulge in the glass just below the A7 cone so that the cone cannot be forced through the hole in the metal washer 5. Three Bourdon pressure gauges (N.P.L. calibrated) were used, reading respectively to 20, 40, and 60 atm.

To fill the piezometer, it was inverted and joined by its cone and a socket (the union being then mercury-sealed) to a system of stopcocks communicating with reservoirs containing the alcohol and mercury and with a vacuum pump. After evacuation it was almost filled with

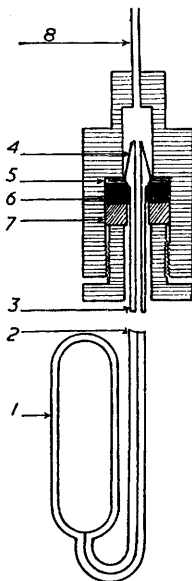


FIG. 1.

- (1) Piezometer, capacity *ca.* 30 ml.
- (2) Capillary, *ca.* 1 mm. i.d. This extends most of the way across the gap of about 40 cm. between the top of the piezometer and the brass head, the upper part of the capillary being calibrated.
- (3) Capillary, *ca.* 3 mm. i.d., sealed to the narrower capillary.
- (4) A7 cone.
- (5) Split brass washer.
- (6) Hard-rubber packing.
- (7) Brass collar.
- (8) Metal outlet to gauges and source of pressure.

alcohol. The important operation of drying the inside of the capillary was effected either before the mercury was admitted by cooling the alcohol and warming the capillary, or else by filling the remaining space of the piezometer with mercury and then cooling the bulb until the mercury had withdrawn almost completely into it, when light petroleum was injected into the capillary and then removed by pumping. The amount of mercury was finally adjusted until, with the piezometer in melting ice, the mercury meniscus in the capillary at atmospheric pressure was near the top of the calibrated section. The separate volumes of the alcohol and mercury in the piezometer were calculated from the sum of the masses of the two liquids and the known internal volume of the piezometer.

To measure the compressibility of an alcohol, the pressure was increased in stages to *ca.* 10, 20, 30, 40, and 45 atm. and decreased in stages to *ca.* 35, 25, 15, and 5 atm. At the end of each pressure change, after about 15 min. had elapsed for thermal equilibrium to be restored, the distance between the mercury meniscus and a suitable reference mark was measured to 0.01 mm. Each pressure was measured to *ca.* 0.1%. In calculating the pressure on the liquid, allowance was made for the changing height of mercury in the capillary. To calculate the compressibility of the alcohol it was necessary to allow for the compression of the mercury and for the bulging of the piezometer under pressure. The correction for the mercury was small as its volume was usually only between 2 and 3 ml. The correction for the bulging of the vessel amounted to between 8 and 13% of the total observed volume change. It was accurately determined by carrying out a series of compressibility determinations on water. From the observed volume

decreases were deducted the contraction due to the mercury and that due to the water, the latter being calculated from the compressibility results for water at 0° of Marshall, Staveley, and Hart.² A plot of the resulting values for the increase in volume of the piezometer against the applied internal pressure gave a good straight line of slope 0.2488×10^{-3} ml./atm. There was no detectable difference between the points measured in compression and those measured in decompression.

The coefficient of expansion α of each alcohol was measured from *ca.* -14° to *ca.* $+14^\circ$. The apparatus was that described by Burlew,³ but for greater precision a larger dilatometer was used of capacity *ca.* 10 ml. This made it necessary to control the temperature of the dilatometer to $\pm 0.001^\circ$. The thermostat consisted of a 6 l. Dewar vessel filled with a water-alcohol mixture. This could be cooled fairly rapidly with solid carbon dioxide to the lowest temperature required. Cold gaseous oxygen was then sent from a reservoir of liquid oxygen through a vacuum-jacketed tube into a copper tube in the water-alcohol mixture, so that, without any heating, the thermostat just cooled. The oxygen was boiled off from the reservoir by electrical heating; fine control of the rate at which the thermostat tended to cool was easily achieved by controlling this current. To maintain temperature constancy, counter-heating was then applied to the thermostat fluid by use of a toluene regulator with a Sunvic proportionating head in the usual way. The temperature could be held constant to $\pm 0.001^\circ$ for as long as necessary. Temperatures were measured with the platinum resistance thermometer used by Marshall, Staveley, and Hart.² After the dilatometer had been filled with alcohol as described by Burlew,³ it was cooled to 0° with the tip immersed in mercury. When equilibrium had been reached, the mercury reservoir was removed and a small empty reservoir fixed to the outlet to catch the mercury expelled when the dilatometer warmed to room temperature before being weighed. The volumes of alcohol and mercury in the dilatometer were estimated from the total weight of alcohol and mercury filling it at 0°, the known capacity of the dilatometer, and the measured density of each alcohol at 0°. With the tip of the dilatometer dipping under mercury contained in a small bucket, the dilatometer was cooled to the starting temperature of *ca.* -16° and allowed to reach thermal equilibrium, which required about 1 hr. The bucket was then removed and replaced by a weighed bucket containing some mercury and, the temperature of the thermostat having been measured, the thermostat was heated about 4°. After thermal equilibrium had been restored and the new temperature recorded, the bucket was removed, dried in a desiccator containing mercury, and replaced by a similar weighed bucket also containing mercury. The whole process was then repeated. Much more consistent results were obtained by using a bucket with enough mercury to enable the top of the dilatometer to be dipped into it just before the removal of the bucket

All values refer to 0°. $\rho_{\text{obs.}}$ is the measured density of the alcohol in g./ml., $\rho_{\text{lit.}}$ the value selected by Timmermans. β_0 is the isothermal compressibility at 1 atm. in atm.^{-1} , b the quantity in the equation $\beta = \beta_0 - bp$, where p is the pressure on the alcohol in atm. in excess of 1 atm. α_0 is the coefficient of expansion of the alcohol at 0°, a the quantity in the equation $\alpha = \alpha_0 + at$, where t is the temperature in °C. The two equations are valid to *ca.* 45 atm. and from -14° to $+14^\circ$ respectively. The ratio α_0/β_0 is in atm./deg.

	Methanol	Ethanol	Propanol	Butanol
$\rho_{\text{obs.}}$	0.81000	0.80624	0.81949	0.82461
$\rho_{\text{lit.}}$	0.81005	0.80625	0.81926	0.82472
$10^6\beta_0$	108.3 ± 0.59	100.0 ± 0.60	85.42 ± 0.38	82.03 ± 0.36
10^6b	0.18 ± 0.024	0.168 ± 0.023	0.144 ± 0.014	0.120 ± 0.014
$10^3\alpha_0$	1.1522 ± 0.0002	1.0505 ± 0.0003	0.9618 ± 0.0004	0.9116 ± 0.0004
10^6a	1.53 ± 0.02	1.75 ± 0.03	0.99 ± 0.04	0.94 ± 0.04
α_0/β_0	10.63 ± 0.06	10.50 ± 0.06	11.26 ± 0.05	11.11 ± 0.05
	Pentanol	Hexanol	Heptanol	Octanol
$\rho_{\text{obs.}}$	0.83085	0.83284	0.83652	0.83895
$\rho_{\text{lit.}}$	0.82897	0.83285	—	0.84216
$10^6\beta_0$	78.08 ± 0.29	75.63 ± 0.46	71.38 ± 0.47	69.06 ± 0.43
10^6b	0.109 ± 0.005	0.157 ± 0.008	0.076 ± 0.009	0.080 ± 0.016
$10^3\alpha_0$	0.8594 ± 0.0008	0.8456 ± 0.0005	0.8273 ± 0.0006	0.8151 ± 0.0005
10^6a	1.71 ± 0.09	0.81 ± 0.02	1.44 ± 0.02	0.80 ± 0.02
α_0/β_0	10.87 ± 0.04	11.18 ± 0.07	11.59 ± 0.07	11.80 ± 0.07

than by using empty buckets into which the expelled mercury was allowed to drop, because part of a drop occasionally remained clinging to the tip. The capacity of the dilatometer was

² Marshall, Staveley, and Hart, *Trans. Faraday Soc.*, 1956, **52**, 19.

³ Burlew, *J. Amer. Chem. Soc.*, 1940, **62**, 690.

measured by finding the weight of mercury needed to fill it completely at 0°. The thermal expansion of the dilatometer was determined by finding the amount of mercury expelled from the mercury-filled dilatometer when heated over a range of *ca.* 30° and then using Sears's results for the density of mercury.⁴

The densities of the alcohols at 0° were measured in a pycnometer of capacity *ca.* 10 ml. of the type described by Kohler and Rott,⁵ which is particularly suitable for density measurements below room temperature.

The alcohols were dried either by refluxing them over freshly roasted quicklime or over aluminium amalgam, and they were then fractionated in a 25-plate or a 40-plate column. A middle fraction was collected over less than 0.05° for the first four alcohols and less than 0.4° for the second four. The measured densities at 0° are in the Table where they are compared with the values selected by Timmermans.⁶ The most serious discrepancy is for octanol. However, with our density figures, the increment in molar volume for the step heptanol–octanol is 16.32 ml., which is only 0.02 ml. less than the average increment for the three preceding steps, whereas Timmermans's value for octanol gives the considerably smaller value of 15.75 ml. for the heptanol–octanol increment. This suggests that the density value selected by Timmermans may be too low.

RESULTS

The compressibility results were evaluated as follows. If on increase of pressure from p_1 to p_2 (p 's being the measured pressures acting on the alcohol *in excess of 1 atm.*) there was a decrease of v in the volume of the alcohol, and if V was the *mean* of the volumes of the alcohol at the initial and final pressures, then the quantity $v/[V(p_2 - p_1)]$ was evaluated as the compressibility β of the alcohol at a pressure p , where $p = (p_1 + p_2)/2$. For each alcohol β was a linear function of p , so that $\beta = \beta_0 - bp$. The values of $10^6\beta_0$ and 10^6b , obtained by the method of least squares are given in the Table with their probable errors. β_0 is the true isothermal compressibility of an alcohol at 0°/1 atm.

As regards the evaluation of the coefficient of expansion, the most accurate density data over a limited range of temperature for a pure liquid can usually be accurately represented by a power series in the temperature t up to terms in t^3 . We have taken such density equations for a few selected liquids, and made the following comparison. (1) We have evaluated the true coefficient of expansion α at some temperature t (°C) at which the volume of a given mass of the liquid is V , where $\alpha = (1/V)(\partial V/\partial t)_p$. (2) We have evaluated the volumes of the liquid V_1 and V_2 at temperatures t_1 and t_2 respectively, where $t_1 = t - 2$ and $t_2 = t + 2$, and then calculated the *mean* coefficient of expansion $\bar{\alpha}$ given by the expression $\bar{\alpha} = (V_2 - V_1)/2(V_1 + V_2)$. The difference between $\bar{\alpha}$ and the true coefficient of expansion α never exceeded one part in 10^4 . Since in our coefficient of expansion determinations the average temperature increment was *ca.* 4°, we have evaluated α as follows. If v was the expansion of the alcohol on heating from t_1 to t_2 , and if V_m was the volume of the alcohol at $t = (t_1 + t_2)/2$, then α at t was taken to be $v/V_m(t_2 - t_1)$. V_m could be estimated with sufficient accuracy from the known volume of the alcohol at 0° and a mean α for the whole range studied. The values of α so obtained were always a linear function of t . The values of $10^3\alpha_0$ and 10^4a in the equation $\alpha = \alpha_0 + at$, calculated by the method of least squares, are given in the Table with their probable errors. α_0 is the required value of the coefficient of expansion at 0°.

DISCUSSION

The systematic errors in the compressibility and coefficient of expansion values should not exceed 0.5% and 0.2% respectively. Since however one and the same apparatus has been used for all measurements of one kind, a comparison of the ratios of α_0/β_0 should not be significantly affected by systematic errors. The values of this ratio in atm./deg. are given in the Table with their probable (random) errors.

In Fig. 2 $\alpha_0/\beta_0 = (\partial S/\partial V)_T$ is plotted against the number of carbon atoms in the alcohol molecule. The trend in $(\partial S/\partial V)_T$ as the chain length increases is not simple. The first

⁴ Sears, *Proc. Phys. Soc.*, 1913, **26**, 95.

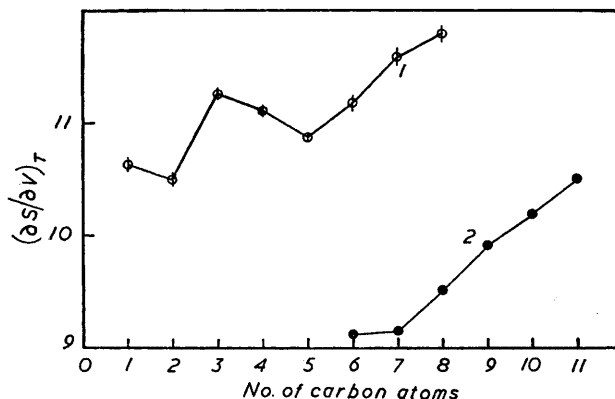
⁵ Kohler and Rott, *Monatsh.*, 1954, **85**, 703.

⁶ Timmermans, "Physico-chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

four alcohols might be said to show an alternation effect, but instead of the increase from butanol to pentanol needed to continue this alternation there is a decrease. Only from pentanol onwards does $(\partial S/\partial V)_T$ increase continuously. The only other systematic measurements of α and β on the liquid members of a homologous series seem to be those made many years ago by Bartoli⁷ on the normal paraffins from hexane to hexadecane at *ca.* 23°. It is difficult to assess the reliability of his figures. His values of α show discrepancies of up to *ca.* 2% with more modern determinations. However, his values being used throughout for consistency, $(\partial S/\partial V)_T$ for the normal paraffins increases at about the same rate as for the alcohols from pentanol to octanol. (See Fig. 2, in which is plotted the ratio α/β for hexane to undecane. The trend shown by these hydrocarbons continues for the others studied by Bartoli.)

It might be argued that the thermodynamic properties of the alcohols should be compared not at a constant temperature but on a corresponding-states basis. It is difficult to decide what this should be for such strongly associated liquids. One possibility, following Bauer, Magat, and Surdin,⁸ is to make the comparison at such a temperature T for each alcohol that $(T - T_m)/(T_c - T_m)$ is a constant, where T_m and T_c are respectively the melting and critical points. It so happens that at 0° this function of temperature is

FIG. 2. Plot of the quantity $(\partial S/\partial V)_T = \alpha/\beta$ (atm./deg.) against the number of carbon atoms per molecule for (1) normal primary alcohols and (2) normal paraffins. The vertical lines on the points for the alcohols represent the estimated probable errors.



almost equal for ethanol and propanol. It is just for these two that $(\partial S/\partial V)_T$ differs most. Moreover, for methyl, butyl, and higher alcohols the same value of $(T - T_m)/(T_c - T_m)$ would correspond to temperatures above 0°. Since α/β decreases as the temperature rises, the corresponding values of $(\partial S/\partial V)_T$ would rise from ethanol to a maximum at propanol and then decrease. It therefore seems unlikely that a comparison on this basis would prove helpful.

In comparing on the basis of the Hildebrand rule the entropies of vaporization of the normal paraffins, Staveley and Tupman⁹ noted that the vaporization entropies first decreased with increasing chain length, and then increased. They suggested that, for the earlier members of the series, increased chain length actually produced greater disorder in the liquid owing to the increased number of configurations available to the molecules, but that with the longer molecules the greater tendency towards a parallel alignment leads to an increase in internal order which is reflected in increasing values for the entropy of vaporization. Perhaps opposing factors of this kind operate with the lower primary alcohols, but since with the latter an essential part in the intermolecular relations is played

⁷ Bartoli, *Rend. reale Ist. lombardo sci.*, 1895, **28**, 1141.

⁸ Bauer, Magat, and Surdin, *Trans. Faraday Soc.*, 1937, **33**, 81.

⁹ Staveley and Tupman, *J.*, 1950, 3597.

by the hydrogen bonding which is lacking with the hydrocarbons there is no reason why there should be a close similarity between the trends in the physical properties for the two series. The large increase in $(\partial S/\partial V)_T$ on passing from ethanol to propanol followed by a decrease in this quantity for the next two stages has no parallel in the vaporization entropies of the normal paraffins.

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