79. *Solutions of Alcohols in Non-polar Solvents. Part II.* Volume Relations in Dilute Solutions of Primary Alcohols in Benzene, Heptane, and* cyclo*Hexane.*

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An apparatus is described for the accurate determination of the small volume changes which occur when one liquid is mixed with a much larger quantity of another. Measurements have been made at 20° of the volume changes occurring when the first six primary alcohols, and *n*-octanol and *n*-decanol, are mixed with benzene, heptane, and *cyclo*hexane, to give solutions in which the mole-fraction, x, of the alcohol is between 0·005 and 0·035. For the benzene solutions, the volume increase v per mole of alcohol is an almost linear function of x. In the other two solvents, the v–x plots are curved, their shapes being consistent with the view, based on spectroscopic work, that in the concentration range concerned the alcohols associate to trimers. In benzene, however, it is possible that association starts by the production of even larger aggregates, perhaps tetramers.

By extrapolation, values of the partial molar volumes at infinite dilution ($\bar{V}_\infty$) of the alcohols in the three solvents have been derived. Whereas in heptane, $\bar{V}_\infty$ increases by almost constant increments on passing from one alcohol to the next (from ethanol to decanol), this is not so in benzene and *cyclo*hexane, where the increments show an alternation. The observed effects are compared with those which would be expected if, from pentanol onwards, the monomeric alcohol molecules tend to coil into a cyclic configuration. The results are not inconsistent with this possibility, but do not definitely prove it.

IN Part I * of this series it was suggested on the basis of solubility studies that, in dilute benzene solutions of the normal primary alcohols, the interaction between the hydroxyl group and the surrounding benzene molecules underwent a change when the hydrocarbon group of the alcohol molecule became sufficiently long to be capable of screening the hydroxyl group. The evidence indicated that this change took place on passing from butanol to pentanol, and it was tentatively proposed that the monomeric molecules of pentanol and higher alcohols, unlike those of their predecessors, had a tendency to adopt a coiled configuration in benzene solution, this tendency being perhaps encouraged by the cyclic character of the solvent molecules. Since the spatial requirements of a flexible molecule in such an environment might differ according to whether it was coiled or extended, it seemed worth while to examine the partial molar volumes at infinite dilution of alcohols of increasing chain length. The partial molar volumes at infinite dilution can be found by extrapolation either from density determinations on progressively more dilute solutions, or from measurements of the volume changes which occur when dilute solutions are made by mixing appropriate amounts of the alcohol and solvent. Numerous values of the densities of dilute solutions of alcohols in non-polar solvents have been published (mostly in connection with dipole moment measurements), but with the possible exception of those of Harms (*Z. physikal. Chem.*, 1943, **53**, *B*, 280) they are far too inaccurate to be of any use for the present purpose, and even Harms's results scarcely extend to sufficiently low concentrations. Association of alcohol molecules in non-polar solvents becomes appreciable at such low concentrations that the measurements must be made on very dilute solutions if extrapolation is to have any value and then, to achieve the accuracy sought, very precise density determinations are essential. In a benzene solution containing ethyl alcohol at a mole-fraction of 0·01, an error in the density of 1 : 80,000 would involve an error of approximately 0·1 c.c. in the apparent molar volume of the solute. We have accordingly preferred to measure the volume change on mixing of alcohol and solvent, since this is virtually a direct measurement of the difference between the volume of a given mass of the pure alcohol and its effective volume in the dilute solution.

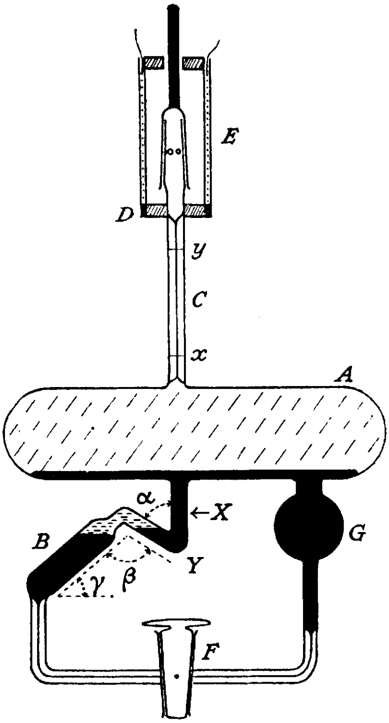
* Part I, *J.*, 1951, 2516.

Whereas, as stated in Part I, attempts to determine the solubility in non-polar solvents other than benzene were not successful, no such limitation applies to the study of volume changes on mixing. With a view to studying the influence which the shape of the solvent molecules may have on the configuration adopted by flexible solute molecules, we have used benzene, *n*-heptane, and *cyclo*hexane as solvents. The alcohols examined were those from methanol to *n*-hexanol inclusive, *n*-octanol and *n*-decanol.

EXPERIMENTAL

In the experiments with any one alcohol in any one solvent, the mole fraction of the alcohol was usually between 0·005 and 0·035. Keyes and Hildebrand (*J. Amer. Chem. Soc.*, 1917, **39**, 2126) have described an apparatus for measuring volume changes on mixing liquids. Preliminary experiments showed that, while this apparatus serves admirably if the quantities of the two liquids are not very different, it is not suitable when one of them is very much larger than the other as in our work, for it becomes necessary to construct the container for the solute from capillary or semi-capillary tubing, and the operation of mixing is then excessively difficult. The apparatus shown in Fig. 1 was therefore devised. The capillary *C* was approximately 7 cm. long, and was provided with reference marks, *x* and *y*. The cross-section between *x* and *y* had been carefully determined, and was approximately 2×10^{-2} sq. cm. The total internal volume up to one of the marks on the capillary, determined by filling the vessel with water and weighing it, was ~110 c.c. The capacity of the barrel *A* was about 85 c.c. and that of the bulb *B* about 7 c.c. The angles α, β, and γ were 60°, 105°, and 45° respectively. The apparatus was held securely in a metal frame so that it could be rocked (in the plane of the paper) about an axis through the point *X*. It was immersed in a thermostat to just above the base of the jacket *E*. This jacket was electrically heated so that the temperature inside it was held constant a few degrees above the thermostat temperature (20°), thus eliminating the possibility of any vapour condensing from the meniscus in the capillary into the space above it. The ground glass cap above the capillary was greased with a lubricant made from dextrin, mannitol, and glycerol.

FIG. 1. *Apparatus for determining volume changes on mixing, shown containing the alcohol, hydrocarbon, and mercury before mixing.*



The vessel was filled as follows. Into the weighed empty vessel was introduced sufficient mercury to fill completely the lower part of the vessel with an overflow of several c.c. into the barrel *A*, and the vessel was then weighed again. Care had to be taken to see that no air bubbles were trapped by the mercury (they could easily be removed by rocking the vessel). The tap *F* was closed, and the vessel turned clockwise through about 60° and clamped. The alcohol was then introduced from a pipette provided with a tap and a long thin metal capillary with a very small opening. This capillary was inserted into the vessel until its tip reached the point *Y*, and the required quantity of alcohol forced into the bulb by applying pressure to the pipette. This operation could be conducted without introducing any air bubbles, but degassed alcohol was used so that any small bubbles admitted into *B* would dissolve. The weight of the alcohol trapped in the bulb *B* was found from the change in weight of the pipette. The vessel was now clamped in its frame in a vertical position, the cone greased, and the jacket *E* fitted on the rubber collar *D*. The vessel was placed in the thermostat and a suitable current passed through the heating coil *E*. The solvent, previously degassed, was then blown into the barrel *A* through a metal capillary, until finally its meniscus was just above the reference mark *x*. Dry air was blown into the capillary above the meniscus to ensure that the glass walls of the upper part of the vessel would be free from any drops of adhering solvent, and the vessel was then closed with the ground-glass cap. When temperature equilibrium had been attained, the position of the meniscus relative to one of the reference marks x and y was read with a travelling microscope. Before every reading, the ground-glass cap was turned to be open momentarily to the atmosphere. The volume of solvent in the apparatus was found by subtracting the volume of alcohol and mercury from the total volume of the vessel.

For mixing of the liquids, the vessel was tilted anticlockwise through 45° and the tap F opened, whereupon the alcohol was displaced by mercury into the barrel. (The function of the bulb G was to ensure that in this operation the head of mercury would not fall to such an extent that expulsion of the alcohol from B would be incomplete.) In order to wash out the bulb B, the vessel was tilted until it was inclined at 45° to the right, whereupon the solution entered B.

TABLE 1. *Volume Changes.*

(v is the volume increase in c.c. occurring on mixing of one mole of alcohol with sufficient solvent to give a solution in which the mole-fraction of the alcohol is x.)

Alcohol	Solvent								
Methanol	Benzene	v	0·76	0·73	0·77	0·68			
		10^3x	9·0	16·4	22·1	27·6			
	Heptane	v	6·83	5·41	5·33	3·85			
		10^3x	4·8	10·8	14·3	27·3			
	*cyclo*Hexane	v	3·31	3·17	2·81	2·65			
		10^3x	8·3	13·2	25·1	34·9			
Ethanol	Benzene	v	2·18	2·15	1·93	1·35			
		10^3x	11·7	16·1	22·0	33·9			
	Heptane	v	6·80	5·76	4·33	3·78			
		10^3x	6·9	12·1	25·1	33·7			
	*cyclo*Hexane	v	6·96	5·67	3·93	3·26			
		10^3x	6·1	12·9	24·4	34·6			
Propanol	Benzene	v	1·97	1·80	1·63	1·53			
		10^3x	8·4	17·1	24·4	33·8			
	Heptane	v	6·05	5·60	4·64	3·43	3·18		
		10^3x	6·3	8·2	12·8	27·8	34·5		
	*cyclo*Hexane	v	6·03	5·18	4·15	3·60			
		10^3x	4·5	9·7	19·3	27·5			
Butanol	Benzene	v	2·46	2·29	2·12	2·00			
		10^3x	6·3	13·7	20·6	28·2			
	Heptane	v	5·66	4·55	3·29	3·05			
		10^3x	4·9	11·3	22·0	26·8			
	*cyclo*Hexane	v	7·01	5·46	4·22	3·70			
		10^3x	3·9	8·5	14·7	24·4			
Pentanol	Benzene	v	2·73	2·60	2·49	2·35	2·21		
		10^3x	7·4	9·9	12·4	21·9	27·4		
	Heptane	v	5·02	5·11	4·87	4·15	3·50	2·86	1·84
		10^3x	4·1	4·8	5·9	8·3	11·1	17·7	26·8
	*cyclo*Hexane	v	5·98	5·31	4·51	3·66			
		10^3x	3·9	8·3	13·8	24·5			
Hexanol	Benzene	v	3·20	2·95	2·79	2·54			
		10^3x	5·1	12·2	18·6	25·5			
	Heptane	v	5·03	3·90	2·64	2·27	1·78		
		10^3x	4·6	8·6	15·6	22·4	29·6		
	*cyclo*Hexane	v	6·42	5·97	4·95	4·90	4·12		
		10^3x	4·6	6·6	12·3	13·6	20·5		
Octanol	Benzene	v	3·82	3·61	3·41	3·34			
		10^3x	4·0	11·6	14·6	18·8			
	Heptane	v	3·61	3·12	1·90	1·36			
		10^3x	4·1	7·2	14·0	20·4			
	*cyclo*Hexane	v	7·00	6·22	5·19	4·15			
		10^3x	2·9	5·3	10·5	18·7			
Decanol	Benzene	v	4·63	4·55	4·54	4·41			
		10^3x	2·6	8·5	13·9	17·4			
	Heptane	v	2·27	1·64	1·06	0·43			
		10^3x	5·3	10·0	14·6	22·0			
	*cyclo*Hexane	v	7·52	7·37	7·09	6·21	5·80		
		10^3x	2·6	3·0	4·6	8·0	14·2		

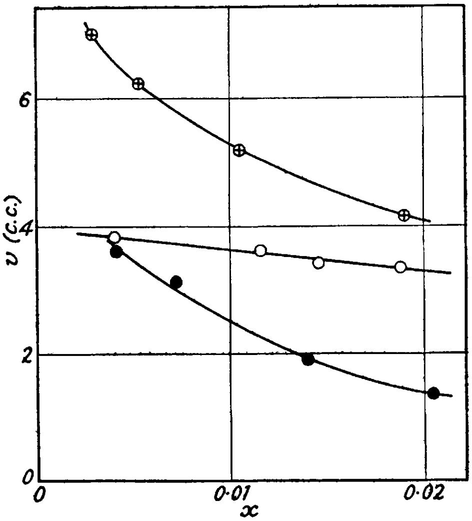
Tap *F* was closed, and the vessel turned anticlockwise through 90°. When the tap was opened, mercury refilled *B*. After repetition of this washing-out process, the tap was finally closed, and the vessel rocked for 5 minutes. The new position of the meniscus relative to a reference mark was then measured. The washing-out was repeated and the vessel rocked for a further 5 minutes, until constant readings were obtained, although usually there was no further change after the first period of shaking.

In a blank run in which a small amount of benzene (instead of an alcohol) was mixed with benzene, the apparent volume change did not exceed 10^{-4} c.c. It may be noted here that one disadvantage of the Keyes and Hildebrand apparatus, compared with ours, is that with the former, which has two capillaries, the measurement of a volume change requires twice as many readings. Moreover, with our apparatus it is easier to ensure that all readings of a set are made with the liquid under the same pressure, and in addition, since the space above the capillary is always saturated with solvent vapour, there is no possibility of solvent being lost by evaporation.

All measurements were made at 20·00° and the temperature of the thermostat was kept constant to $\pm 0{\cdot}001°$. The necessity for careful control of the temperature will be evident from the fact that the volume changes measured were sometimes as small as 6×10^{-3} c.c.

The lower alcohols up to and including pentanol were purified by fractionation and finally dried over aluminium amalgam. The three higher alcohols were first purified by fractional crystallisation, dried in the same way, and distilled. Their b. p.s at 760 mm. were: methanol, 64·59°; ethanol, 78·36°; propanol, 97·15°; butanol, 117·61°; pentanol, 137·92°; hexanol, 157·12°; octanol, 193·2°; and decanol, 229·84°. The benzene used was a sulphur-free sample which had been purified by fractional crystallisation and fusion until its m. p. was 5·35°, corresponding to 0·26 mole-% of impurity. *cyclo*Hexane was free from benzene by treatment with nitrating mixture, and then fractionally crystallised. The m. p. of the final dry material was 6·05°, representing 0·26 mole-% of impurity. The heptane used was certified by the National Bureau of Standards as being 99·8% pure on a molar basis. As it blackened mercury slightly, it was shaken with mercury until reaction ceased and then distilled from phosphoric anhydride.

FIG. 2. *Plots of the volume increase per mole* (v) *of octanol, against the mole fraction* (x) *of the alcohol in the resulting solution.*



○ Benzene; ● heptane; ⊕ *cyclo*hexane.

Results.—The results are given in Table 1.

DISCUSSION

For every alcohol in the concentration range studied the plot of *v* against *x* is apparently linear for the benzene solutions, whereas for the mixtures with heptane and *cyclo*hexane it is a curve convex to the *x* axis. This is illustrated in Fig. 2, in which are plotted the results for octanol.

From the experimentally determined relation between *v* and *x* for any one system, we may hope to draw conclusions about the value of v_1 (*i.e.*, the value of *v* when $x = 0$), and about the progressive association of the alcohol with increasing concentration, on which the shape of the *v*–*x* curve must depend. We shall consider the second matter first, since if, on the basis of assumptions about the association which are reasonable and consistent with other data, it proves possible to account for the experimental *v*–*x* curves, we then have a rational basis for the extrapolation to give v_1.

The very careful spectroscopic studies of solutions of alcohols in non-polar solvents carried out by Mecke and his collaborators (Kreuzer and Mecke, *Z. physikal. Chem.*, 1941, **49**, *B*, 309; Hoffmann, *ibid.*, 1943, **53**, *B*, 179; Mecke and Nückel, *Naturwiss.*, 1943, **21**,

248) have shown that the association begins by the formation, not of dimers, but of trimers. Their work also indicates that in the region of comparatively small alcohol concentrations with which we are concerned, it is a permissible approximation to neglect the formation of higher polymers, and also to apply the law of mass action in its ideal form to the equilibrium between monomer and trimer. Consider a solution containing (1 — x) mole of solvent, and x mole of alcohol (*i.e.*, a total quantity of alcohol of xM g., where M is the g.-mol. weight of the monomer). If a fraction α of the alcohol A is associated to the trimer, then for the equilibrium constant K (on a mole-fraction basis) of the association $3A \rightleftharpoons A_3$, we have

$$K = \frac{\alpha(1 - 2\alpha x/3)^2}{3x^2(1 - \alpha)^3} \approx \frac{\alpha}{3x^2(1 - \alpha)^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Let us suppose that addition of M g. of alcohol to a large quantity of solvent would increase the volume by v_1 c.c. if all the alcohol were monomeric in the resulting solution, and by v_3 c.c. if all the alcohol were in the trimeric form. Let us further assume that v_1 and v_3 are constant (for a given alcohol in a given solvent at a fixed temperature) over the whole concentration range concerned (up to $x \approx 0{\cdot}035$). Then the actual volume increase v per mole of alcohol is

$$\begin{aligned} v &= (1 - \alpha)v_1 + \alpha v_3 \\ &= v_1 - \alpha(v_1 - v_3) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2) \end{aligned}$$

Hence there is a simple relation between the values of v and α for any three alcohol concentrations. Thus

$$\frac{v_{0\cdot005} - v_{0\cdot01}}{v_{0\cdot005} - v_{0\cdot015}} = \frac{\alpha_{0\cdot01} - \alpha_{0\cdot005}}{\alpha_{0\cdot015} - \alpha_{0\cdot005}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where the subscripts are the values of x, *e.g.*, $v_{0\cdot01}$ is the volume increase in c.c. when one mole of alcohol is mixed with solvent to give a solution in which its mole fraction is 0·01 and its degree of association to trimers is $\alpha_{0\cdot01}$. For solutions of the alcohols in heptane and *cyclo*hexane, smoothed curves were drawn through the experimental points, from which $v_{0\cdot005}$, $v_{0\cdot01}$, and $v_{0\cdot015}$ were obtained. These gave the following values for the quantity on the left-hand side of equation (3) (the first figure of each pair refers to the *cyclo*hexane solutions, the second to the heptane solutions): methanol, 0·54, 0·555; ethanol, 0·55, 0·55; propanol, 0·575, 0·585; butanol, 0·665, 0·560; pentanol, 0·585, 0·610; hexanol, 0·610, 0·605; octanol, 0·615, 0·615; decanol, 0·565, 0·57. The mean value for *cyclo*hexane solutions is 0·59, and for heptane solutions 0·58. Divergencies from these are probably not greater than can be attributed to experimental error, except perhaps for butanol in *cyclo*hexane. If the value for this system is omitted, the mean of the *cyclo*hexane figures is 0·575.

Likewise, the quantity $\frac{v_{0\cdot005} - v_{0\cdot015}}{v_{0\cdot005} - v_{0\cdot025}}$ has a mean value of 0·67 (with extremes of 0·61 and 0·71) for the alcohols in heptane, and for methanol, ethanol, propanol, and pentanol in *cyclo*hexane a mean value of 0·635, with extremes of 0·67 and 0·62. (For butanol, the ratio is 0·79. The remaining three alcohols were not studied at sufficiently high concentrations for this ratio to be evaluated.)

Hoffmann (*loc. cit.*) has obtained spectroscopically a value for the equilibrium constant at 21·5° for the trimerisation of methanol in carbon tetrachloride. Combination of this with the heat of association given by Mecke and Nückel (*loc. cit.*) leads to a value of K of equation (1) of $2{\cdot}23 \times 10^3$ at 20°. Hoffmann further found that neither the nature of the alcohol (at least for the primary alcohols) nor that of the non-polar solvent (excluding benzene) has any very pronounced effect on the association. With this value of K, $\frac{\alpha_{0\cdot01} - \alpha_{0\cdot005}}{\alpha_{0\cdot015} - \alpha_{0\cdot005}}$ is 0·58, and $\frac{\alpha_{0\cdot015} - \alpha_{0\cdot005}}{\alpha_{0\cdot025} - \alpha_{0\cdot005}}$ is 0·66. In view of the agreement between these figures and those for the corresponding ratios involving v, we may say that for the *cyclo*hexane and heptane solutions, the dependence of v on x is consistent with the formation from the monomeric alcohol of trimers, with an equilibrium constant for the association of $\sim 2{\cdot}2 \times 10^3$ at 20°. We have accordingly calculated v_1 and $(v_1 - v_3)$ from equation (2), using the experimental values of $v_{0\cdot005}$ and $v_{0\cdot01}$ and the α values corresponding to $K = 2\cdot23 \times 10^3$ ($\alpha_{0\cdot005} = 0\cdot116$, $\alpha_{0\cdot01} = 0\cdot265$). The figures for v_1 and v_3 so obtained are recorded in Table 2. The v–x curve for butanol in *cyclo*hexane shows more pronounced curvature than any other, and it may be that one or more of the experimental points is considerably in error. Accordingly, for this system two sets of values are given for v_1 and v_3. Those marked *a* are derived from $v_{0\cdot005} - v_{0\cdot01}$; those marked *b* from $v_{0\cdot01}$ and $v_{0\cdot015}$.

TABLE 2. *Molar Volumes.*

(V_0 is the molar volume of the pure alcohol, $\bar{V}_\infty$ the partial molar volume in infinitely dilute solution. v_1 or v_3 is what the volume increase would be on mixing of one mole of alcohol with a large amount of solvent if the alcohol in the resulting solution were entirely monomeric or trimeric respectively. All volumes are in c.c. and refer to 20°.)

	Pure alcohols		In *cyclo*hexane			
	V_0	$\Delta V_0/CH_2$	v_1	v_3	$\bar{V}_\infty$	$\Delta\bar{V}_\infty/CH_2$
Methanol	40·49	17·87	3·75	2·05	44·25	22·25
Ethanol	58·36	16·43	8·15	0·5	66·5	14·95
Propanol	74·79	16·74	6·65	0·8	81·45	17·95 ^{a} 17·15 ^{b}
Butanol	91·53	16·60	7·9 ^{a} 7·05 ^{b}	−2·6 −0·35	99·4 ^{a} 98·6 ^{b}	15·3 ^{a} 16·1 ^{b}
Pentanol	108·13	16·61	6·6	0·75	114·7	17·1
Hexanol	124·74	2 × 16·52	7·05	0·45	131·8	2 × 16·6
Octanol	157·78	2 × 16·48	7·15	0	164·95	2 × 16·7
Decanol	190·75		7·65	2·6	198·4	

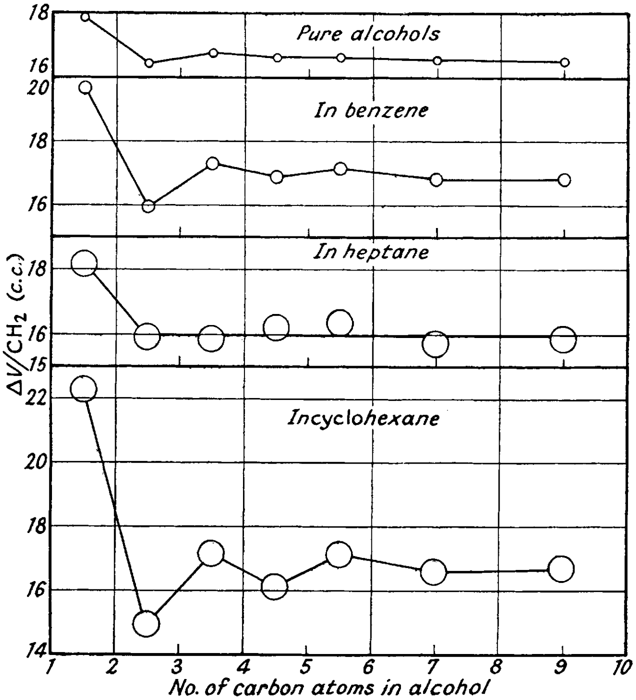
	In heptane				In benzene		
	v_1	v_3	$\bar{V}_\infty$	$\Delta\bar{V}_\infty/CH_2$	v_1	$\bar{V}_\infty$	$\Delta\bar{V}_\infty/CH_2$
Methanol	7·65	0·8	48·15	18·1	0·8	41·3	19·65
Ethanol	7·90	1·25	66·25	15·9	2·6	60·95	15·95
Propanol	7·35	−0·65	82·15	15·85	2·1	76·9	17·25
Butanol	6·45	0	98·0	16·2	2·6	94·15	16·85
Pentanol	6·05	−2·7	114·2	16·35	2·85	111·0	17·1
Hexanol	5·8	−2·25	130·55	2 × 15·7	3·35	128·1	2 × 16·8
Octanol	4·2	−2·25	162·0	2 × 15·85	3·95	161·75	2 × 16·8
Decanol	2·95	−2·1	193·7		4·65	195·4	

That the v–x curves for *cyclo*hexane and heptane solutions can be satisfactorily interpreted in terms of trimerisation cannot be regarded as a proof in itself that the association is in fact of this kind. The curves can be accounted for almost equally well if it is assumed that dimerisation is involved and a suitable equilibrium constant adopted. On this latter basis, v_1 values are obtained which are larger than those recorded in Table 2, and which are roughly the same as those obtained by free-hand extrapolation of the v–x curves. (On the trimerisation hypothesis, the v–x curves must have an initial slope of zero.) These larger values of v_1, however, still stand in the same relation to one another as those in Table 2, and their use would not alter the qualitative conclusions we shall draw from the values in Table 2.

For the benzene solutions the relation between v and x over the concentration range investigated is linear within experimental error, and we have therefore estimated the v_1 values given in Table 2 by direct extrapolation. We shall later show that these linear relations may, in a sense, be fortuitous. But as the slope of the experimental lines is comparatively small and the solutions examined are very dilute, it is unlikely that linear extrapolation gives values of v_1 which are seriously in error, or that its use leads to a false impression of the relation between the true values of v_1 for the different alcohols.

In Table 2, $\bar{V}_\infty$ is the partial molar volume of an alcohol at infinite dilution ($= v_1 + V_0$, where V_0 is the molar volume of the pure alcohol). $\Delta\bar{V}_\infty/CH_2$ is the increment in $\bar{V}_\infty$ on passage from one alcohol to its homologue. The changes in these increments (and also those in V_0) are shown in Fig. 3. It is difficult to assess the error in the values of $\Delta\bar{V}_\infty/CH_2$. The circles for the *cyclo*hexane and heptane solutions have been drawn with a radius representing 0·4 c.c., corresponding to an error of ±0·2 c.c. in v_1. Those for benzene solutions have a radius representing 0·2 c.c., corresponding to an error of ±0·1 c.c. in v_1. For butanol in *cyclo*hexane, as already explained, there is greater uncertainty in v_1. We have chosen the lower figure in Table 2 to evaluate the two increments which depend on it. The higher value of v_1 would make still more pronounced the differences between these increments and those which precede and follow them.

FIG. 3. *The relations between the increments per* CH_2 *group in* V_0 *and in* V_∞ *in the three solvents as the homologous series is ascended.*



Each point is plotted midway between the number of carbon atoms in the two alcohols concerned. For the steps hexanol–octanol and octanol–decanol, the average increments have been plotted.

The following conclusions emerge from Table 2 and Fig. 3. (1) In all three solutions, and for the pure alcohols, the increment for methanol–ethanol is larger than for any subsequent step. (2) For the lower alcohols, the increments in V_0 show a slight alternation. This is more pronounced with the values of $\Delta\bar{V}_\infty/CH_2$ in benzene, and still more so in *cyclo*hexane. By contrast, in heptane, these increments from ethanol onwards are almost constant (within the probable limits of our experimental error). (3) If the step methanol–ethanol is excluded, the average increments in molar volume per CH_2 group are : in benzene, 16·8 c.c. ; pure alcohols, 16·55 c.c. ; in *cyclo*hexane, 16·5 c.c. ; in heptane, 15·95 c.c. In other words, the space required by a CH_2 group in the hydrocarbon chain of a monomeric alcohol molecule is greatest in benzene solution, about the same in *cyclo*hexane as for the pure alcohol, and least in heptane, where it is almost identical with the corresponding quantity for the normal paraffins. (The average value of $\Delta V_0/CH_2$ from pentane to *n*-decane is 15·9 c.c.) (4) The mean value of $(v_1 - v_3)$ for *cyclo*hexane solutions is ~6·3 c.c., and for heptane solutions ~7·0 c.c. Hence an alcohol molecule entering one of these solvents as a member of a trimer requires effectively considerably less space than if it enters as a monomer. In fact, if the higher alcohols could dissolve in heptane exclusively as trimers there would be an appreciable volume contraction. (5) In *cyclo*hexane and heptane, the values of v_3 (at least as far as hexanol) show an alternation.

We shall consider briefly the bearing of these results on the question which prompted the work, namely, whether monomeric alcohol molecules with sufficiently long chains tend to adopt coiled configurations in a favourable environment. If, in benzene and *cyclo*hexane solution, this tendency first appears with pentanol (the lowest alcohol capable of simulating a six-membered ring), then since this should lead to particularly economical packing of the alcohol molecules among the solvent molecules, we should expect a relatively low value of $\bar{V}_\infty$ for this alcohol and a correspondingly small value of $\Delta\bar{V}_\infty/CH_2$ for the step butanol–pentanol. Molecules of the next higher alcohol, hexanol, could presumably either tend to adopt a quasi-seven-membered ring structure, or a six-membered ring with one end of the molecule overlapping the ring. Some idea of the consequence of the second possibility may be obtained by considering the relationship of the molar volumes of a series of liquids such as benzene, toluene, *o*-xylene, and 1 : 2 : 3-trimethylbenzene; or *cyclo*hexane, methyl*cyclo*hexane, and ethyl*cyclo*hexane. For the three steps of the first group, the values of $\Delta V_0/CH_2$ are 17·55, 15·1, and 12·8 c.c.; for the second group, the increments are 19·7 and 17·6 respectively. The addition of a methyl group as a protuberance on a very symmetrical molecule causes a relatively large increase in V_0; further addition of a methyl group, or the enlargement of the first into an ethyl group, is accompanied by an appreciably smaller change in V_0 (cf. the abnormally large increments in V_0 and $\bar{V}_\infty$ for the step methanol–ethanol). If therefore a monomeric hexanol molecule in benzene or *cyclo*hexane tends to coil into a quasi-six-membered ring with one end of the molecule overlapping, we should expect to find this reflected in a relatively large $\bar{V}_\infty$, giving a large increment in $\bar{V}_\infty$ for the step pentanol–hexanol. But we should also expect that $\Delta\bar{V}_\infty/CH_2$ would be smaller for the next step, hexanol–heptanol.

These predictions are in fact consistent with the results summarised in Table 2 and Fig. 3. But the results cannot be regarded as proving the hypothesis, partly because of the omission of experiments on heptanol (which unfortunately could not be carried out in the time available for this work), and partly because the lower alcohols up to butanol show variations in $\Delta\bar{V}_\infty/CH_2$ as striking as those for the alcohols from butanol onwards. Nevertheless, the contrast between the trend in $\bar{V}_\infty$ for heptane solutions on the one hand, and that in benzene and, more strikingly, in *cyclo*hexane solutions on the other, shows how subtle the relation between solute and solvent molecules in such solutions must be, since, depending on the geometry of the solvent molecules and on the structure of the solvent, the partial molar volumes at infinite dilution of solutes such as primary alcohols sometimes show a steady increase per CH_2 group, and sometimes an alternating increase.

There is some evidence that alternation is also displayed by the apparent molar volumes of the alcohols in the trimeric state. The quantity $(V_0 + v_3)$ is the apparent volume occupied by the formula weight in grams of an alcohol if present in solution wholly as trimers. The increments in this quantity are :

	C_1–C_2	C_2–C_3	C_3–C_4	C_4–C_5	C_5–C_6	C_6–C_8	C_8–C_{10}
*cyclo*Hexane ...	16·3	16·75	15·6	17·7	16·3	2 × 16·3	2 × 17·8
Heptane	18·3	14·55	17·4	13·9	17·05	2 × 16·5	2 × 16·55

In both of these series, there is a regular alternation, at least as far as hexanol, and it is to be noted that this is now more marked for the heptane solutions, in which, by contrast, the values of $\Delta\bar{V}_\infty/CH_2$ are almost constant. Moreover, those steps (such as propanol–butanol), which in *cyclo*hexane give the smaller increments, give the larger increases in $(V_0 + v_3)$ in heptane. As it may be felt that little reliance can be placed on the values of $(V_0 + v_3)$ (since in the evaluation of v_3 a fixed mean value of the association constant was assumed), we may point out that the experimental v–x curves for the lower alcohols in these two solvents shown an alternation which is quite independent of the way in which they have been analysed. The curvature of the plot for methanol is much less marked for *cyclo*hexane than for heptane; for ethanol, however, the heptane curve is the flatter of the two; for propanol, the position is again reversed, and so on. This alternation in the relative steepness of the two curves certainly persists up to, and including, pentanol.

There remains the question of the interpretation of the apparently linear relation between v and x for the alcohols in benzene. This can be accounted for if it is supposed that in the concentration range in question the alcohols are beginning to associate to dimers. But there seems no doubt from the spectroscopic work of Mecke and his collaborators (*loc. cit.*) that dimerisation does not occur at all. There is other evidence to support this. The careful freezing-point measurements by Peterson and Rodebush (*J. Phys. Chem.*, 1928, **32**, 709) on very dilute solutions of ethanol in benzene showed that up to a mole-fraction of $\sim$0·004, the molecular weight is normal within $\sim$2%. Accurate dielectric-constant measurements at 24·5° gave no indication of any association up to a mole fraction of 0·01 (Hoecker, *J. Chem. Physics*, 1936, **4**, 431). On the other hand, Beckmann's early freezing-point studies (*Z. physikal. Chem.*, 1888, **2**, 715) on more concentrated solutions showed that the apparent molecular weight starts to increase rapidly in the neighbourhood of $x = 0·01$, and is nearly double the normal value when $x = 0·04$. These facts suggest that the association of alcohols in benzene begins by the formation of higher aggregates than dimers (or even trimers), and, though Beckmann's results are not really sufficiently accurate for a definite decision to be made on this point, they do in fact agree better with the formation of tetramers than of trimers. We may also note that recently Weltner and Pitzer (*J. Amer. Chem. Soc.*, 1951, **73**, 2606) have pointed out that the virial coefficient data for methanol vapour are best interpreted in terms of tetramer formation. Furthermore, the aggregates formed in benzene, whatever they may be, differ from the trimers produced in other non-polar solvents in that, whereas the latter (from the rapid decrease of the molar polarisation as the concentration rises from zero) must have small or zero moment, the polymers in benzene must be highly polar, since the molar polarisation increases with alcohol concentration.

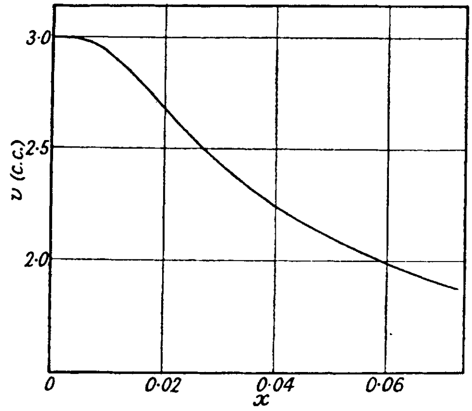


FIG. 4. *The course which would be taken by a plot of* v *against* x *if the alcohol was associated to tetramer (for assumptions see text).*

Fig. 4 is a plot of v against x calculated on the assumption that the alcohol is associated exclusively to tetramers. v_1 (the volume increase if a mole of alcohol goes into solution as the monomer) has been taken as 3 c.c.; v_4 (the volume increase if the same amount of alcohol dissolves as the tetramer) as 1 c.c.; and the equilibrium constant, *i.e.* (tetramer concn.)/(monomer concn.)^4, has been assumed to be 10^4 on a mole-fraction basis. The choice of these values is arbitrary, but the values for the two volumes are not unreasonable, nor, in the light of Beckmann's freezing-point data, is that for the equilibrium constant. It will be seen that the association of the alcohol is very slight when x is less than 0·01 : it is a little less than 1% when $x = 0·006$. Over the range $x \gtrsim 0·01$ to $\gtrsim 0·035$ (*i.e.*, the concentration range covered in our experiments) the curve is nearly linear with a mean slope about equal to the average of those of the experimental lines. Finally, the shape of the curve at higher concentrations is very similar to that derived from Harms's density determinations (*loc. cit.*). At least, therefore, we may say that the available data, as a whole, are not inconsistent with the possibility that the initial association of the alcohols in benzene is by tetramer formation. It is hoped to carry out further experiments to test this provisional conclusion.

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[*Received, September* 28*th*, 1951.]