38. *Solutions of Alcohols in Non-polar Solvents. Part III.* The Viscosities of Dilute Solutions of Primary Alcohols in Benzene, Heptane, and* cyclo*Hexane.*

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Measurements have been made at 20° C, with a precision of 0·01—0·02%, of the relative viscosities of dilute solutions in benzene, *cyclo*hexane, and heptane of the following normal primary alcohols: methanol to hexanol inclusive, octanol, and decanol. Only for heptane do the curves of specific viscosity against concentration fall regularly in the order of increasing molecular weights of the alcohols. Before the results can yield any information about changing configurations of the alcohol solute molecules with increasing chain length, allowance has to be made for the effect on the viscosity of the volume changes on mixing of solute and solvent. An attempt has been made to do this by supposing that for small volume changes the viscosity is to a first approximation a pure volume function. The corrected curves of viscosity against concentration for the solutions in *cyclo*hexane and benzene then fall in a regular sequence, but it seems that solutions of butanol, pentanol, and hexanol in benzene have smaller viscosities than might be expected from the behaviour of the other alcohols, which may be due to coiling of the molecules of these three alcohols in this solvent.

The results have also been discussed in relation to association of alcohols in non-polar solvents. The observed viscosity–concentration relations confirm a previous conclusion that the dimerisation stage is omitted. It seems probable that the first polymers formed are trimers.

PART I of this series (Staveley, Johns, and Moore, *J.*, 1951, 2516) dealt with measurements of the solubility and heat of solution of water in dilute solutions of alcohols in benzene. These measurements appeared to show that a change takes place in the interaction between the alcohol and benzene molecules on passing from butanol to pentanol, and it was tentatively suggested that in benzene solution the molecules of pentanol (and of higher alcohols) tend to adopt coiled configurations whereby the hydroxyl group is to some extent screened. Then (see Part II *) experiments were carried out on the volume changes on mixing of primary alcohols with benzene, heptane, and *cyclo*hexane, values being obtained for $\overline{V}_\infty$, the partial molar volumes of the alcohols in these three solvents at infinite dilution. In heptane, $\overline{V}_\infty$ increased by an almost constant amount from one alcohol to the next, whereas in benzene and *cyclo*hexane the increments per CH_2 group showed an alternation. These findings were not inconsistent with the possibility that the molecules with longer chains tend to adopt a coiled configuration in the solvents having cyclic molecules, but they could not be regarded as confirming this suggestion. They showed, however, that the volume relations between the members of homologous series in dilute solution depend on the nature of the solvent, and it was therefore thought worthwhile to examine viscosities, particularly since they can be measured very accurately and because, although our knowledge of the dependence of the viscosity of liquids on their structure is not as yet very detailed, the viscosities of dilute solutions must depend on the interaction between solution and solvent molecules; thus, if this interaction is affected by factors such as whether the number of carbon atoms in the alcohol molecule is odd or even, or whether the alcohol molecule tends to be coiled or not, these should in turn affect the viscosity. Admittedly

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* Part II, Staveley and Spice, *J.*, 1952, 406.

the viscosity will in any case by influenced by the volume requirements of the solute molecules in the solution, and this will be considered in the Discussion.

EXPERIMENTAL

Owing to the association of alcohols in non-polar solvents, quite dilute solutions must be used to provide information relating to monomeric alcohol molecules. At room temperature, alcohols are effectively unassociated in benzene only at mole fractions <0·01, and in heptane and *cyclo*hexane below the even smaller mole fractions of ~0·003 and 0·0015 respectively (Wolf, *Trans. Faraday Soc.*, 1937, **33**, 179). Ideally, the viscosity measurements would have been made on solutions no more concentrated than these, but the viscosity differences between solution and solvent would then have been exceedingly small. It was therefore necessary to make measurements over a wider range of concentration, and to proceed by extrapolation to infinite dilution. For heptane and benzene, the range of mole fractions covered was 0·005 to 0·03, and in *cyclo*hexane 0·002 to 0·025. It was considered necessary to aim at an accuracy of 0·02% in the viscosity measurements. Two viscometers were used, of the Ostwald type constructed as described by Washburn and Williams (*J. Amer. Chem. Soc.*, 1913, **35**, 737). The total volume of liquid contained in each was about 66 c.c., of which about 25 c.c. discharged during a run through a capillary tube of internal diameter ~0·5 mm., and length about 20 cm. According to the solvent and viscometer used, the flow times at 25° C varied from 17 to 45 min. These times were measured to 0·1 sec. with a hand-operated stop-watch. Usually the difference between the flow times for two consecutive runs agreed to within 0·2 sec. or better. Only very occasionally did they differ by as much as 0·5 sec. With every new solution or with an experiment with pure solvent, the first timed run was preceded by an untimed run.

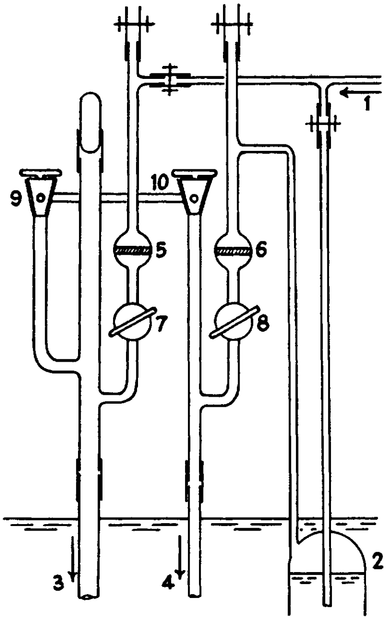


FIG. 1. *Fittings for each viscometer.* 1, Inlet for clean, dry, compressed air; 2, saturator; 3, to reservoir of viscometer; 4, to capillary of viscometer; 5, 6, sintered-glass filters; 7, 8, 9, 10, taps.

In a series of experiments with any one alcohol in any one solvent, a known volume of pure solvent was introduced into one of the viscometers, and after temperature equilibrium had been reached the flow-time was determined, 2—3 measurements being made. Solutions of the alcohol were made up in the viscometer itself, beginning with the most dilute solution. To do this, a known weight of the pure alcohol was added from a weight pipette to the solvent in the reservoir of the viscometer *via* its wide limb. The liquids were mixed by bubbling dry dust-free air (saturated with solvent at the same temperature) down the capillary limb and up into the reservoir for 10—15 min. Then some of the solution was removed in a dropping pipette (read to 0·001 c.c.), so that the volume of the liquid in the viscometer would remain the same for each run. When the flow times for the solution so prepared had been measured, the next solution was made by the addition of more alcohol, and so on. Almost always, the complete series of experiments on any one alcohol in any one solvent was completed in a day.

Great care was taken to avoid contamination of the viscometers by dust, and in particular to see that the air used for mixing the solutions and also for pumping liquid from the reservoir of a viscometer to the bulb above the capillary was free from dust. Instead of taking air from the laboratory compressor, air was compressed by means of a hand-pump into a large glass bottle and maintained there at constant pressure. When an air-stream was required, it was taken from the bottle and passed successively through sulphuric acid, pumice soaked in sulphuric acid, phosphoric oxide, cellulose gauze, and a small sintered-glass filter. Fig. 1 shows the arrangement of these filters and of the necessary taps and connections at the top of each viscometer. The taps numbered 9 and 10 were necessary in order to put the spaces in the two tubes of the viscometer in direct communication before the start of each run. The rubber connections were made of new tubing which had been thoroughly washed. A strip-light just above the thermostat not only provided illumination but also (combined with suitable screening) kept the air at a temperature a little above that of the thermostat, thus eliminating the risk of the condensation of solvent from the air-stream in its passage from the saturator to the viscometer.

All experiments were carried out at 20° ± 0·005° c, this being the temperature at which the measurements of the volume change on mixing had previously been made. The viscometers were mounted on holders of the type described by Applebey (*J.*, 1910, 2000), which were screwed to a thick block of seasoned wood bolted to a rigid steel framework. This method of vibration-free mounting enabled the viscometers to be replaced always in exactly the same positions.

The viscometers were cleaned with concentrated nitric acid, distilled water, alcohol, and ether, and dried with a stream of dry, dust-free air.

The samples of the alcohols and of heptane used were those with which the experiments described in Part II were carried out. Benzene and *cyclo*hexane were purified in the same way as before, but the final products were slightly purer, having f. p.s 5·46° and 6·07° respectively.

RESULTS

The results are given in Table 1. For each solution is recorded (1) the mole fraction x of the alcohol, $\times 10^2$ (2) the density of the solution, calculated from the figures given in Part II for the

TABLE 1.

For (1), (2), (3), (4), see text.

Solutions in heptane

Methanol

(1)	0·47	1·14	1·81	2·46	3·01
(2)	0·68369	0·68374	0·68383	0·68398	0·68409
(3)	0·9977	0·99545	0·9942	0·99315	0·9925
(4)	−2·35	−4·45	−5·6	−6·45	−6·9

Ethanol

(1)	0·75	1·10	1·62	2·14	2·63
(2)	0·68378	0·68386	0·68399	0·68414	0·68430
(3)	0·9973	0·99635	0·9962	0·99585	0·9958
(4)	−2·6	−3·45	− 3·4	−3·5	−3·45

Propanol

(1)	0·53	1·10	1·58	2·08	2·26
(2)	0·68387	0·68412	0·68436	0·68461	0·68489
(3)	0·99855	0·9988	0·9992	1·0000	1·0014
(4)	−1·2	−0·55	0·2	1·3	3·1

Butanol

(1)	1·05	1·54	2·02	2·50	2·91	3·44	3·92
(2)	0·6843	0·6846	0·6850	0·6853	0·6856	0·6860	0·6864
(3)	0·9997	1·0004	1·00185	1·00453	1·0082	1·0100	1·0132
(4)	0·6	1·7	3·7	6·8	11·0	13·5	17·1

Pentanol

(1)	0·52	1·04	1·55	2·11	2·53	2·90	3·37
(2)	0·68409	0·68454	0·68500	0·68554	0·68594	0·68629	0·68675
(3)	0·9999	1·00315	1·0056	1·0093	1·01245	1·0157	1·01935
(4)	0·5	4·4	7·5	12·0	15·8	19·5	23·9

Hexanol

(1)	0·50	1·15	1·69	2·21	2·76	3·35
(2)	0·68408	0·68485	0·68545	0·68602	0·68666	0·68734
(3)	1·0012	1·0060	1·0109	1·0164	1·0228	1·0302
(4)	1·8	7·7	13·5	19·9	27·2	35·7

Octanol

(1)	0·45	0·93	1·38	1·92	2·43	2·96
(2)	0·68421	0·68501	0·68567	0·68649	0·68729	0·68811
(3)	1·0037	1·0098	1·0169	1·0267	1·0361	1·0473
(4)	4·45	11·7	19·9	30·9	41·6	54·1

Decanol

(1)	0·48	0·99	1·48	2·01
(2)	0·68456	0·68551	0·68643	0·68745
(3)	1·0075	1·01925	1·0323	1·0471
(4)	8·8	21·95	36·45	52·85

TABLE 1. (*Continued*).

Solutions in benzene

Methanol

(1)	0·47	1·09	1·53	1·99	2·50
(2)	0·87888	0·87858	0·87837	0·87815	0·87791
(3)	0·9956	0·9903	0·9872	0·9843	0·98135
(4)	−4·7	−10·3	−13·6	−16·8	−20·0

Ethanol

(1)	0·53	1·10	1·64	2·11	2·63
(2)	0·87866	0·87820	0·87780	0·87745	0·87709
(3)	0·9954	0·9916	0·9883	0·9857	0·9836
(4)	−5·1	−9·4	−13·1	−16·2	−18·6

Propanol

(1)	0·50	1·00	1·50	2·02	2·56
(2)	0·87868	0·87827	0·87787	0·87746	0·87705
(3)	0·9971	0·9952	0·9929	0·9917	0·9907
(4)	−3·4	−5·7	−8·5	−10·2	−11·6

Butanol

(1)	0·51	1·04	1·51	2·02	2·47	2·95
(2)	0·87861	0·87811	0·8777	0·8772	0·8768	0·8764
(3)	0·9969	0·9947	0·9933	0·9929	0·9929	0·9938
(4)	−3·7	−6·5	−8·2	−9·3	−9·7	−9·3

Pentanol

(1)	0·57	1·09	1·63	2·15	2·67	3·24
(2)	0·87851	0·87798	0·87744	0·87694	0·87645	0·87593
(3)	0·9980	0·9970	0·9967	0·9975	0·9993	1·0013
(4)	−2·6	−4·2	−5·2	−4·9	−3·7	−2·3

Hexanol

(1)	0·53	1·04	1·69	2·10	2·63	3·29
(2)	0·87850	0·87779	0·87721	0·87679	0·87626	0·87563
(3)	0·9991	0·99915	1·0011	1·0040	1·0070	1·0116
(4)	−1·6	−2·3	−1·1	1·4	3·7	7·6

Octanol

(1)	0·51	1·04	1·56	2·02
(2)	0·87843	0·87775	0·87711	0·87657
(3)	1·0038	1·0087	1·0144	1·0226
(4)	3·0	7·1	12·1	19·7

Decanol

(1)	0·55	1·07	1·60	2·14
(2)	0·87827	0·87751	0·87674	0·87598
(3)	1·0072	1·0155	1·0259	1·0381
(4)	6·3	13·7	23·2	34·4

Solutions in cyclo*hexane*

Methanol

(1)	0·34	0·83	1·23	1·62
(2)	0·77823	0·77814	0·77808	0·77802
(3)	0·9954	0·99015	0·9866	0·9844
(4)	−4·7	−10·1	−13·7	−16·0

Ethanol

(1)	0·18	0·49	0·78	1·04
(2)	0·77821	0·77807	0·77798	0·77791
(3)	0·9969	0·9924	0·9890	0·9870
(4)	−3·3	−7·9	−11·4	−13·5

Propanol

(1)	0·27	0·53	0·81	1·05	1·51
(2)	0·77822	0·77817	0·77813	0·77811	0·77808
(3)	0·9965	0·99295	0·9907	0·9889	0·9870
(4)	−3·6	−7·2	−9·5	−11·3	−13·2

Butanol

(1)	0·23	0·52	1·06	1·49	1·86
(2)	0·77823	0·77819	0·77821	0·77824	0·77826
(3)	0·9963	0·9931	0·9910	0·9902	0·9900
(4)	−3·8	−7·1	−9·1	−9·9	−10·1

Pentanol

(1)	0·29	0·57	1·15	1·70
(2)	0·77828	0·77828	0·77833	0·77842
(3)	0·9963	0·9940	0·9933	0·9935
(4)	−3·7	−6·0	−6·7	−6·4

Hexanol

(1)	0·51	1·01	1·54	2·01	3·14
(2)	0·77831	0·77839	0·77851	0·77864	0·77908
(3)	0·9946	0·9952	0·9978	1·0011	1·0107
(4)	−5·4	−4·6	−1·9	1·6	11·7

Octanol

(1)	0·29	0·54	0·86	1·16
(2)	0·77835	0·77843	0·77855	0·77868
(3)	0·9985	0·99935	1·0019	1·0062
(4)	−1·5	−0·5	2·2	6·7

Decanol

(1)	0·27	0·54	0·80
(2)	0·77840	0·77852	0·77864
(3)	1·0008	1·0040	1·0097
(4)	1·0	4·3	10·1

volume changes on mixing, in g./c.c. (3) the ratio of the observed time of flow for the solution to that for the pure solvent, each time being the mean of two, and sometimes three figures, (4) $10^3 \times$ the value of the specific viscosity $\eta_{\text{sp.}}$, where $\eta_{\text{sp.}} = (\eta_{\text{soln.}} - \eta_{\text{solv.}})/\eta_{\text{solv.}} = (\eta_{\text{soln.}}/\eta_{\text{solv.}}) - 1 = (\rho_{\text{soln.}}\, t_{\text{soln.}}/\rho_{\text{solv.}}\, t_{\text{solv.}}) - 1$, where ρ and t denote density and time of flow respectively. The values, 0·6837, 0·8701, and 0·7783 g./c.c., were chosen for the densities at 20° of heptane, benzene, and *cyclo*hexane respectively. Since it is the ratio of the density of a solution to that of the solvent which is important, the choice of slightly different values for the densities of the pure solvents has no significant effect on $\eta_{\text{sp.}}$.

In Figs. 2, 3, and 4 the values of $\eta_{sp.}$ are plotted against x, the mole fraction of the alcohol, for solutions in heptane, benzene, and *cyclo*hexane respectively. Data on solutions sufficiently dilute for comparison with our results exist only for propyl alcohol in benzene at 22° (Andrade and Spells, *J. Sci. Instr.*, 1932, **9**, 316; Spells, *Trans. Faraday Soc.*, 1936, **32**, 530). These results have been reproduced in Fig. 5, together with our own results for the same system at 20°.

Fig. 2.

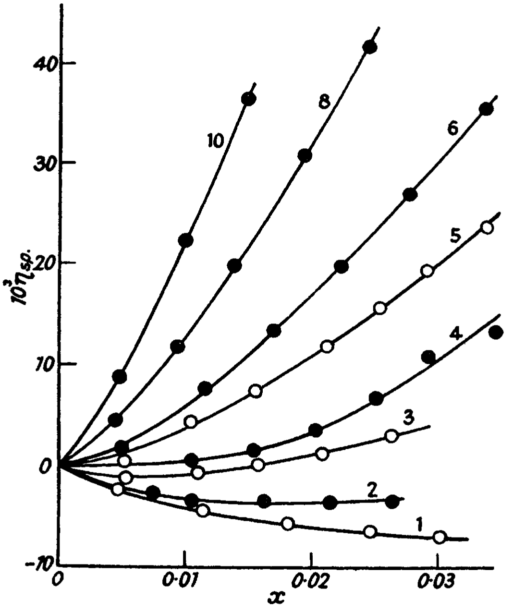


Fig. 3.

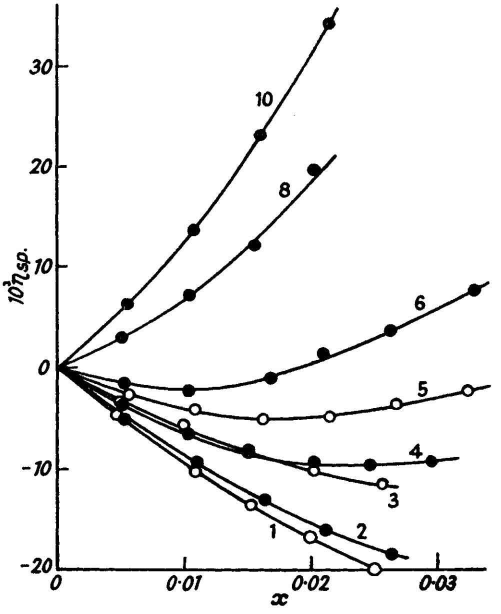
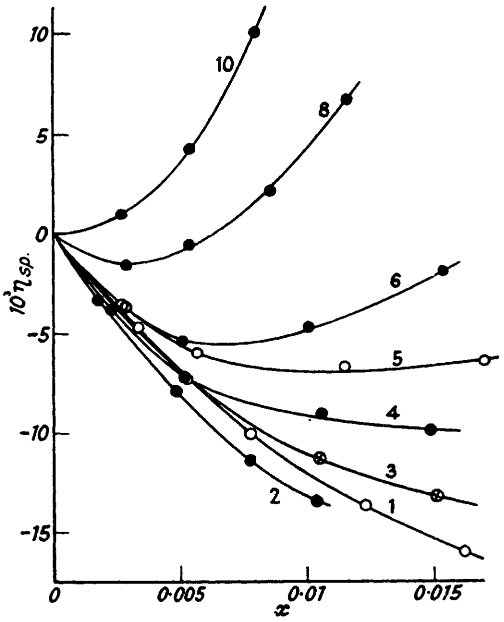


Fig. 4.



Figs. 2, 3, and 4. *Values of* $10^3\eta_{sp.}$, *where* $\eta_{sp.}$ = *the specific viscosity, plotted against* x, *the molar fraction of the alcohol, for solutions in heptane (Fig. 2), in benzene (Fig. 3), and in* cyclo*hexane* (Fig. 4). *The number on each curve is the number of carbon atoms per molecule of the alcohol.*

DISCUSSION

With heptane as solvent, only the lowest three (or possibly four) alcohols initially decrease the viscosity, and over the concentration range studied only the curves for ethanol and propanol (and perhaps butanol) show minima. For benzene solutions, the lower alcohols up to hexanol inclusive at first depress the viscosity, and the curves for butanol, pentanol, and hexanol show minima. So also, from Andrade and Spells's work, does the curve for propanol. For *cyclo*hexane, however, decanol is the only alcohol which does *not* reduce the viscosity at low concentrations, while the curves for the alcohols from pentanol to octanol show minima. These differences are to be correlated with the viscosities of heptane, benzene, and *cyclo*hexane at 20° which are in the ratio 1 : 1·59 : 2·35.

For a set of curves each showing a minimum in the viscosity, this minimum lies at a lower concentration the higher the molecular weight of the alcohol. For the lower alcohols, where the curves shown continuously decrease, minima will exist at higher concentrations, except for methanol in *cyclo*hexane, where the pure alcohol is less viscous than the hydrocarbon. The rapid change of slope of the curves and the appearance of the minima at such low molar fractions of alcohol show rather strikingly that association of the alcohol molecules begins at very low concentrations. Numerous attempts have been made to relate viscosity (or fluidity) of binary liquid mixtures with the viscosities of the two pure components. It is doubtful if there is any value at all in attempting to do this for dilute solutions of alcohols in non-polar solvents where the alcohol begins as monomeric in extremely dilute solution, but rapidly forms polymers as the concentration increases, while the pure alcohol itself is very highly associated.

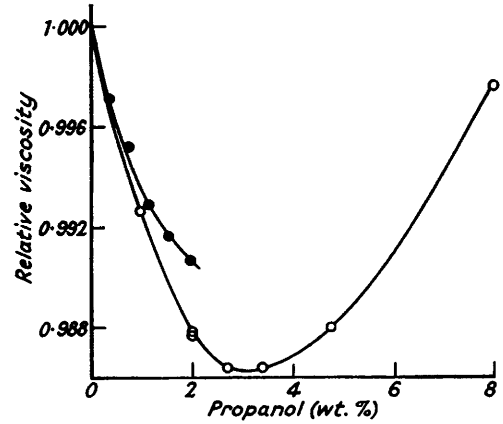


FIG. 5. *Plot of the relative viscosity of solutions of propanol in benzene against the weight percentage of the alcohol.*

●, *This work,* 20° ; ○, *Andrade and Spells's results,* 22°.

It will be seen from Fig. 2 that for heptane solutions the curve for any one alcohol lies between the curves for the two alcohols adjacent to it in the homologous series. But in benzene and *cyclo*hexane this is not always so, and in the initial influence of alcohols on the viscosities of these hydrocarbons we have a property which does not follow the sequence of the homologous series. For a property relating to the liquid state this is unusual. The effect is shown most strikingly for *cyclo*hexane solutions (Fig. 4), where the order of initial slopes is ethanol < butanol < propanol ~ methanol < pentanol < hexanol. For benzene solutions, propanol at first causes a smaller reduction in the viscosity than does butanol.

TABLE 2. *Values of A, the initial slopes of the curves obtained by plotting the corrected specific viscosity against molar fraction of alcohol.*

	Solvent				Solvent		
Alcohol	Heptane	Benzene	*cyclo*Hexane	Alcohol	Heptane	Benzene	*cyclo*Hexane
Methanol......	−0·60	−2·04	−2·06	Pentanol ...	0·13	−1·09	−1·45
Ethanol	−0·48	−1·76	−1·90	Hexanol	0·33	−0·86	−1·15
Propanol	−0·34	−1·54	−1·76	Octanol	0·90	0·32	−0·44
Butanol	−0·16	−1·34	−1·56	Decanol	1·64	1·18	0·58

It is significant that these apparent anomalies can be related to the differences in the volume changes on mixing which were discussed in Part II, or, what amount to the same thing, to the apparent anomalies in the densities of dilute solutions of alcohols in the solvents concerned. Thus, if the densities given in Table 2 for solutions of alcohols in *cyclo*hexane are plotted against the molar fractions of alcohols, the relation between the curves is very much like that in Fig. 4, the order of the initial slopes of the density curves being in fact ethanol $<$ propanol $\sim$ butanol $<$ methanol $<$ pentanol. Alternatively, the point may be made in this way, that the relatively large effects of ethanol and butanol in reducing the viscosity of *cyclo*hexane are due partly to the fact that they mix with this hydrocarbon with a larger volume increase than the other alcohols, while this volume increase is least for methanol, which therefore has a relatively small effect in decreasing the viscosity. Likewise, in benzene solution, the inversion in the sequence of propanol and butanol is due to the fact that, at low alcohol concentrations, propanol mixes with a smaller volume increase than either ethanol or butanol, which leads to a smaller reduction in the viscosity with propanol.

Until allowance has been made for volume effects, therefore, it seems impossible to decide whether the viscosity results give any indication that the alcohol molecules adopt different configurations depending on the length of their chain and the nature of the solvent. Admittedly, the volume effects themselves must depend on the configuration adopted by the alcohol, but it seems permissible to attempt to separate from the overall effect on the viscosity that part due to volume changes when the solution is formed. For example, it is possible, that, by chance, an alcohol in a dilute solution in which it is all monomeric has the same partial molar volume according to whether the molecules are straight or coiled, in which event the volume effects would be the same. But the viscosities for the two cases need not be identical, and any differences between them could be ascribed solely to differences in configuration. On the other hand, if coiling of the solute molecules in itself caused a decrease in viscosity and if at the same time this coiling caused the solvent–solute system to be more expanded, then the second effect would enhance the difference between the viscosities of the solution and the solvent.

Before the specific viscosity curves can be corrected for volume effects, however, we have to decide to what volume the viscosity of any solution is to be corrected, and then how the correction for a given volume change is to be made. For the first one might calculate from the observed value of $\eta_{sp.}$ for a solution at 20° what $\eta_{sp.}$ would be at the same temperature if the solution had been formed from the two liquids with no volume change. This implies, however, that the pure alcohols themselves are a suitable standard for normal behaviour. Actually, they are highly associated, probably into chains of indefinite length, while we are concerned with drawing conclusions, from the properties of dilute solutions in which association is only beginning, about the properties of extremely dilute solutions in which the alcohol is all monomeric. (We may note that, in fact, for the lower alcohols at least, both the viscosities and the molar volumes of the pure alcohols seem to show a slight but definite alternation.) A better choice seems to be to estimate what the viscosity of a given solution would be at the volume which it would have if it had been formed with the same volume change per mole of alcohol as that for the same alcohol on forming a very dilute solution in heptane at the same temperature. The reasons for choosing heptane are : (1) it was shown in Part II that the increments per CH_2 group in the partial molar volumes of the alcohols at infinite dilution are constant within experimental error in heptane (apart from the first step, methanol to ethanol), which is not so for benzene and *cyclo*hexane; (2) as already pointed out, the curves of $\eta_{sp.}$ against alcohol concentration fall in the normal sequence of the alcohols in this solvent, but not in the other two; (3) like the alcohols, it has a straight chain. The second question, namely, how the viscosity is to be corrected for a given volume change, must also be answered rather arbitrarily, since it is known that the viscosity of a liquid is not, in fact, a pure volume function. Nevertheless, it appears that at least at low pressures, and for unassociated liquids, the changes in viscosity brought about by temperature changes and by changes in pressure (if these are not too great) are largely due to the associated volume changes. Unfortunately, there are no data on the effect of compression on the viscosity of heptane and *cyclo*hexane at 20°, and the only datum for benzene is that provided by the early work of Warburg and Sachs (*Wied. Annalen*, 1884, **22**, 518). We may use this as follows to examine how far changes in the viscosity of benzene are determined by volume changes alone. If benzene is cooled from 20° to 19°, the percentage increase in viscosity is 1·54. If benzene at 20° is compressed until its volume is the same as it would be at 19°/1 atm., then according to Warburg and Sachs's results the viscosity would increase by 1·25%. Thus the change in viscosity with temperature is largely but not completely determined by the volume change. However, in view of the absence of information about the effect of pressure on the viscosity of heptane and *cyclo*hexane, the only consistent way in which we can correct for volume effects is by making use of the effect of temperature on the viscosity. The following procedure has, therefore, been adopted.

The actual volume of a solution consisting of $(1 - x)$ moles of solvent and x moles of an alcohol is $V = (1 - x)V_0 + xV_a + xv$, where V_0 and V_a are the molar volumes of pure solvent and alcohol respectively, and v is the observed volume increase on mixing per mole of alcohol. We wish to know the amount $\delta\eta$ by which the observed viscosity of this solution would change if its volume was altered to $(1 - x)V_0 + xV_a + xv_0$, where v_0 is the volume increase on mixing of one mole of the same alcohol with an infinite amount of heptane. That is, we wish to estimate the change $\delta\eta$ in the viscosity if the volume V of one mole of the actual solution is increased by δV, where $\delta V = x(v_0 - v)$. As already indicated, we propose to do this by combining data on the thermal expansion of the liquid with those on the temperature coefficient of viscosity. If the coefficient of expansion of the solution is α, then $\alpha = (1/V)(\partial V/\partial T)_p$, and if we let

$$\beta = \frac{1}{\eta}\left(\frac{\partial\eta}{\partial T}\right)_p, \text{ then } \frac{\delta\eta}{\eta} = \frac{\beta\delta V}{\alpha V} = \frac{\beta}{\alpha V}x(v_0 - v).$$

In the absence of information about the solutions themselves, we shall adopt for α and β the values for the three pure solvents. As the solutions are so dilute, and as we are dealing with a correction term, this approximation cannot involve a serious error. It is also sufficiently accurate to put $V = V_0$, the molar volume of pure solvent, and to regard η in the above equation (the viscosity of the solution) as that of the pure solvent. If, therefore, one mole of the actual solution were increased in volume by δV, the observed specific viscosity of the actual solution, $\eta_{\text{sp.}}$, would increase to $\eta'_{\text{sp.}}$, where $\eta'_{\text{sp.}} = \eta_{\text{sp.}} + \delta\eta/\eta$. The following values of α and β for the three solvents at 20° have been estimated from the data in the International Critical Tables: for benzene, $\alpha = 1{\cdot}237 \times 10^{-3}$, $\beta = -1{\cdot}54 \times 10^{-2}$; for heptane, $\alpha = 1{\cdot}238 \times 10^{-3}$, $\beta = -1{\cdot}16 \times 10^{-2}$; for *cyclo*hexane, $\alpha = 1{\cdot}162 \times 10^{-3}$, $\beta = -1{\cdot}70 \times 10^{-2}$. The necessary values of v_0 and v were taken from the results given in Part II.

The values of $\eta'_{\text{sp.}}$ obtained in this way proved to be quadratic functions of x, the mole fraction of the alcohol, the relation being of the form $\eta'_{\text{sp.}} = Ax + Bx^2$. We are concerned with the values of A, the initial slope of the corrected curve. The slope A, $= (\mathrm{d}\eta'_{\text{sp.}}/\mathrm{d}x)_{x\rightarrow 0}$, is therefore analogous to the quantity sometimes called the intrinsic viscosity. The slope A was evaluated by plotting $\eta'_{\text{sp.}}/x$ against x, drawing the best straight line through the points and extrapolating to $x = 0$. The values of A so obtained are given in Table 2, and are plotted in Figs. 6 and 7 against the number of carbon atoms in the alcohol molecules. It will be seen that, for heptane, the values of A fall on a smooth curve. For this particular solvent this would still be true even if A were calculated from $\eta_{\text{sp.}}$ itself. For *cyclo*hexane, however, the corrections for volume effects have made a radical alteration, for, as shown in Fig. 6, for this solvent also the A values are a smooth function of x, within the limits of experimental error. This is in striking contrast to the relation between the observed relative viscosity–concentration curves of Fig. 4. We may therefore say that there is no evidence from these viscosity studies that in heptane solutions any of the alcohols has an abnormal influence on the viscosity which can be attributed to configurational effects, and the same appears to hold for *cyclo*hexane solutions after allowance has been made for volume effects.

With benzene, however, the position is rather different. It will be seen from Fig. 7 that the points for butanol, pentanol, and hexanol fall below the curve through the other points. Fortunately, for this solvent the plots of $\eta'_{\mathrm{sp.}}/x$ against x, from which the values of A were obtained, give good straight lines of relatively small slope, and we do not think that the failure of the points in Fig. 7 to conform to a smooth curve can be ascribed to experimental error. It therefore appears that when these alcohols are introduced into benzene in the monomeric form they reduce the viscosity more than would be expected from the behaviour of the alcohols which precede and follow them in the homologous series, the effect persisting even when allowance has been made for volume changes. It may be significant that it is for these alcohols that coiling of the molecules might be expected to screen the hydroxyl group, which is known to be capable of quite strong interaction with benzene molecules. It is true that in Part I the coiling of the alcohol molecules in solution was suggested as a possibility which might apply to pentanol and octanol, but not to butanol, to account for the different effects of butanol as compared with the other two alcohols on the heat of solution of water in the medium: whereas here, from Fig. 7, it might be said that, if butanol, pentanol, and hexanol are abnormal in their behaviour, then octanol is normal. But there is no reason, in comparing a series of dilute solutions where the solutes have flexible molecules capable of a variety of configurations, to suppose that the effect of this flexibility on the thermodynamic properties is necessarily a guide to its influence on a property such as viscosity.

FIG. 6.

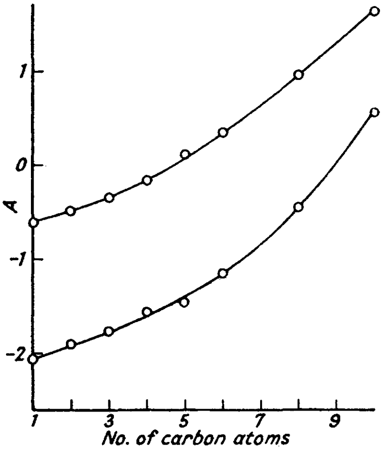


FIG. 7.

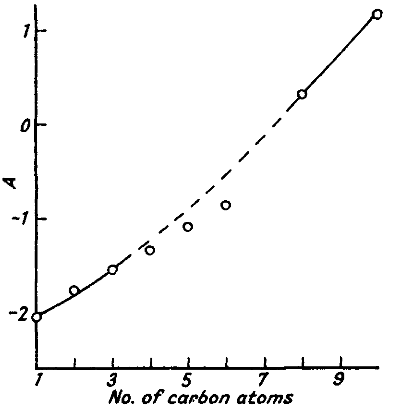


FIG. 6. *Values of* A, $= (\mathrm{d}\eta_{\mathrm{sp.}}/\mathrm{d}x)_{x\to 0}$, *i.e., the initial slope of the corrected curves of specific viscosity against molar fraction of alcohol, plotted against the number of carbon atoms per molecule of the alcohol.* Upper curve, *solutions in heptane.* Lower curve, *solutions in* cyclo*hexane.*

FIG. 7. *Corresponding plot to those in Fig.* 6 *for solutions in benzene.*

We shall finally consider the bearing of our results on the problem of the association of alcohol molecules in non-polar solvents, and we shall show that they support the belief that in this association the dimer stage is omitted, a conclusion first reached from spectroscopic studies (Kreuzer and Mecke, *Z. phys. Chem.*, 1941, **49**, *B*, 309; Mecke and Nückel, *Naturwiss.*, 1943, **21**, 248; Hoffmann, *Z. phys. Chem.*, 1943, **53**, *B*, 179). If we suppose that the association begins by n monomer molecules A aggregating to a polymer A_n, then the equilibrium constant K for the reaction $nA \rightleftharpoons A_n$ is given by $K = \alpha/n(1 - \alpha)^n c^{n-1}$, where α is the fraction of the alcohol associated, and c is the total concentration of the alcohol, expressed in moles/l. as if it were wholly present as monomer. In the early stages of the association we may write

$$(1 - \alpha)^n \approx 1 - n\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and with this approximation we have

$$\alpha = Knc^{n-1}/(1 + Kn^2c^{n-1}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

At the low solute concentrations involved here, we may suppose that the monomer and polymer alter the viscosity of the solvent by amounts proportional to their respective concentrations (with, of course, different proportionality factors for the two species). Since the monomer concentration is $(1 - \alpha)c$, while the polymer concentration is $\alpha c/n$, we have

$$\eta_{\text{soln.}} = \eta_{\text{solv.}} + P(1 - \alpha)c + Q\alpha c/n$$

where P and Q are constants for a given alcohol and a given solvent at a given temperature. Hence

$$\eta_{\text{sp.}} = (\eta_{\text{soln.}} - \eta_{\text{solv.}})/\eta_{\text{solv.}} = Dc + E\alpha c,$$

where $$D = P/\eta_{\text{solv.}}, E = \left(\frac{Q}{n\eta_{\text{solv.}}} - \frac{P}{\eta_{\text{solv.}}}\right).$$

Substituting for α from equation 2 above, we have

$$\eta_{\text{sp.}} = Dc + EKnc^n/(1 + Kn^2c^{n-1})$$

Rearrangement of this last equation gives

$$c^n/(\eta_{\text{sp.}} - Dc) = (1 + Kn^2c^{n-1})/EKn$$

Since the mole fraction x of the alcohols never much exceeds 0·02, we may replace c by x. The value of D is then the initial slope of the curve of $\eta_{\text{sp.}}$ against x, and it can be obtained by drawing tangents at the origin to the curves of Figs. 2, 3, and 4. Subject to the validity of the approximation (1) above, we should find that, if the association begins by dimerisation ($n = 2$), then a plot of $x^2/(\eta_{\text{sp.}} - Dx)$ against x should be linear. If trimers are the first aggregates formed, a plot of $x^3/(\eta_{\text{sp.}} - Dx)$ against x^2 should be linear, while for tetramers this should be true of a plot of $x^4/(\eta_{\text{sp.}} - Dx)$ against x^3. It should be noted that, whichevery possibility actually applies, the corresponding plot should have a positive slope.

In order to apply these criteria of association, we have selected, for each of the three solvents, the five " best " curves of each of Figs. 2, 3, and 4, *i.e.*, those for which the experimental points conform most closely to the smooth curves drawn through them. With the curves rejected for this purpose, the uncertainty in the slope of the initial tangent was thought to be too large. The three plots corresponding to dimers, trimers, and tetramers were then carried out for each of the fifteen systems selected. For twelve of these systems, so far from the plot of $x^2/(\eta_{\text{sp.}} - Dx)$ against x being linear, the values of the former quantity did not even increase continuously with x. For none of the other three systems did this plot give the best straight line. We may therefore conclude that polymerisation does not begin by dimerisation in heptane, benzene, or *cyclo*hexane. For ten of the fifteen systems, the plot for which the points.conformed most closely to straight lines was that corresponding to trimerisation. For the other five systems it was not possible to decide whether the results favoured association into trimers rather than tetramers. The value of the quantity $(\eta_{\text{sp.}} - Dx)$, especially at low concentrations, is rather sensitive to the slope of the initial tangent to the curve. But at least it is fair to say that our results confirm the view that the dimerisation stage is omitted in the association, and on the whole make it probable that, in all three solvents, the first aggregates formed are trimers.

Confirmation of the first of these conclusions comes from a consideration of Fig. 5, in which Andrade and Spells's results for propanol in benzene are plotted. The curve here suggests that the aggregate into which the propanol first associates increases the viscosity of the solution very considerably. If this aggregate is a dimer, it would be a molecule of about the same size and mass as the monomer of hexanol, and might be expected to have much the same effect as the latter on the viscosity. Since our results show that the monomer of hexanol reduces the viscosity of benzene, the inference is that the polymer into which propanol first associates is larger than a dimer.

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