CCLII.—*The Influence of Structure on the Solubilities of Ethers. Part I. Aliphatic Ethers.*

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THE mutual solubilities of ethyl ether and water have been determined with considerable accuracy by several observers, but the corresponding data for other ethers are lacking. In order to reveal the influence of variations in structure on this property, we have measured the solubilities of six isomeric ethers of the formula $C_5H_{12}O$, *viz.*, methyl *n*-butyl, methyl *iso*butyl, methyl *sec.*-butyl, methyl *tert.*-butyl, ethyl *n*-propyl, and ethyl *iso*propyl ethers, and also of the following ethers : methyl *n*- and *iso*-propyl, di-*n*-propyl, propyl *iso*propyl, di-*n*-butyl, and diallyl.

Preparation of Materials.—With the exception of methyl *tert.*-butyl ether, the ethers were most conveniently prepared by Chancel's modification (*Annalen*, 1869, **151**, 305) of the Williamson method, in which an alcohol and an alkyl halide are heated with an excess of solid potassium hydroxide. The latter may be heated first under reflux with the alcohol and the halide then added, or, in other cases, the finely powdered potassium hydroxide may be added gradually to the boiling mixture of the alcohol and the halide. For ethyl *iso*propyl ether, ethyl iodide, *iso*propyl alcohol, and potassium hydroxide were heated in a closed bottle at 100° for several hours. It was found necessary to use only normal alkyl iodides in this reaction, methyl *iso*propyl ether being obtainable, for example, from *iso*propyl alcohol and methyl iodide, but not from methyl alcohol and *iso*propyl iodide. Methyl *tert.*-butyl ether could not be prepared by Chancel's method, and that of Henry (*Rec. trav. chim.*, 1904, **23**, 329) was adopted.

The customary methods of purification of some of these substances were incapable of removing the last traces of the halides used in their preparation. A specimen of ethyl *iso*propyl ether, for instance, after repeated fractional distillation and after boiling for 6 hours with metallic potassium, still contained some iodide, although its density, $d_{4^\circ}^{0^\circ}$ (vac.) 0·7452, was in agreement with the value in the literature. (Compare the difficulty of removing iodides from hydrocarbons; Welt, *Compt. rend.*, 1894, **119**, 743.) The trace of iodide was completely removed by boiling the liquid for 5 hours with diethylamine (15—20% by wt.), and then washing it successively with water, dilute acid, and again with water. The specimen, referred to above, thus purified had, after drying and redistillation, $d_{4^\circ}^{0^\circ}$ (vac.) 0·7440; it was entirely free from halogen, and a repetition of the process of purification caused no further alteration in its density. This method of purification was applied in all cases where an alkyl halide had been used, and the ethers were obtained in a state of greater purity than had previously been attained, as is shown by the fact that the densities observed are in several cases lower than those recorded in the literature.

The following constants were observed (all densities are reduced to a vacuum; the b. p.'s are corrected, but are not to be regarded as such trustworthy criteria of purity as the densities, since often only small quantities of material were available): Methyl *n*-butyl ether, b. p. 70°, $d_{4^\circ}^{0^\circ}$ 0·7635, $d_{4^\circ}^{20^\circ}$ 0·7441; methyl *iso*butyl ether, b. p. 58°, $d_{4^\circ}^{0^\circ}$ 0·7523, $d_{4^\circ}^{20^\circ}$ 0·7311; *methyl* sec.-*butyl ether*, prepared by Chancel's method and purified as described above, b. p. 59°, $d_{4^\circ}^{0^\circ}$ 0·7621, $d_{4^\circ}^{20^\circ}$ 0·7415 (Found: C, 68·8; H, 13·8. $C_5H_{12}O$ requires C, 68·3; H, 13·6%); methyl *tert.*-butyl ether, b. p. 54°, $d_{4^\circ}^{20^\circ}$ 0·7578; ethyl *n*-propyl ether, b. p. 64°, $d_{4^\circ}^{0^\circ}$ 0·7541, $d_{4^\circ}^{20^\circ}$ 0·7330; ethyl *iso*propyl ether, b. p. 53°, $d_{4^\circ}^{0^\circ}$ 0·7440, $d_{4^\circ}^{20^\circ}$ 0·7211; methyl *n*-propyl ether, b. p. 37°, $d_{4^\circ}^{0^\circ}$ 0·7494, $d_{4^\circ}^{13 \cdot 0^\circ}$ 0·7356; methyl *iso*propyl ether, b. p. 32°, $d_{4^\circ}^{0^\circ}$ 0·7383, $d_{4^\circ}^{15^\circ}$ 0·7237; di-*n*-propyl ether, b. p. 91°, $d_{4^\circ}^{20^\circ}$ 0·7360; *n*-propyl *iso*propyl ether, b. p. 83°, $d_{4^\circ}^{0^\circ}$ 0·7597, $d_{4^\circ}^{12 \cdot 5^\circ}$ 0·7474; di-*n*-butyl ether (purchased), b. p. 140°, $d_{4^\circ}^{0^\circ}$ 0·7841; diallyl ether, b. p. 94°, $d_{4^\circ}^{0^\circ}$ 0·8449, $d_{4^\circ}^{20^\circ}$ 0·8260.

Methods of Measurement.—Of the methods available for determining the mutual solubilities of two liquids, that of Hill (*J. Amer.*

Chem. Soc., 1923, **45**, 1143) appeared to be the best, particularly as it gives information as to the composition of both phases of the system; as originally described, however, it involved large vessels and the use of at least 400 c.c. of each liquid, and we therefore reduced the scale of the apparatus in order to adapt it to small quantities of substances (*i.e.*, 4—5 c.c. of each liquid) without appreciable loss of accuracy. The two vessels (Fig. 1) were made from glass tubing of 5 mm. bore, graduated in mm., and were carefully calibrated (in the thermostat) by measuring the volumes of observed weights of pure toluene. The pear-shaped form of the bulbs is important in order to allow the two phases to segregate completely.

FIG. 1.

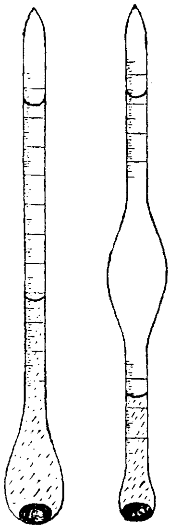
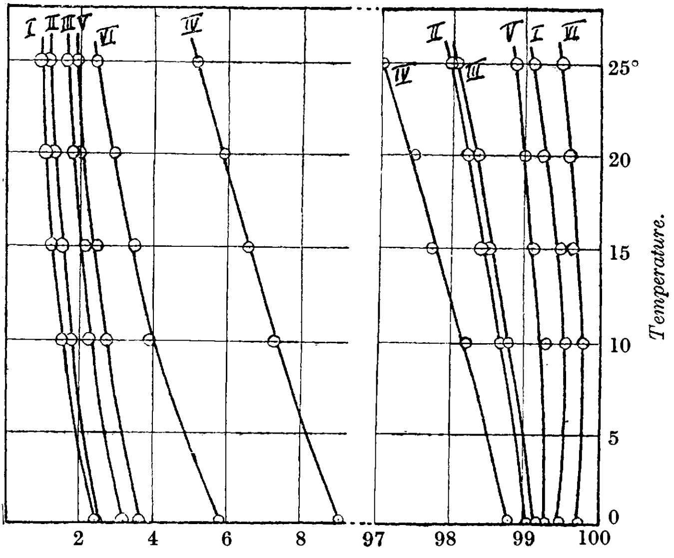


FIG. 2.



Mutual solubilities of isomeric ethers $C_5H_{12}O$ *and water.*

I. *Methyl* n-*butyl ether.*
II. *Methyl* iso*butyl ether.*
III. *Methyl* sec.-*butyl ether.*
IV. *Methyl* tert.-*butyl ether.*
V. *Ethyl* n-*propyl ether.*
VI. *Ethyl* iso*propyl ether.*

It was at first found difficult to secure complete mixing of the phases in these narrow tubes in which an air bubble would not travel. An electromagnetically activated plunger did not bring about rapid mixing, but excellent results were obtained by enclosing in the tube a globule of pure mercury occupying about 1 cm. of the narrow part. When the tube was repeatedly inverted in the thermostat, the mercury travelled down the tube and caused turbulent mixing, complete equilibrium being reached in less than ½ hour.

The thermostat was electrically heated and controlled, the variation being less than 0·01°. Temperatures were read on a thermometer graduated in 0·1° and recently standardised at the National Physical Laboratory. When mixing had been effected, the tubes were attached to a frame and rotated about a vertical axis for 10 minutes to promote the separation of the phases. The tubes were then fixed, preparatory to reading the volumes, in such a position that the glass points, where they had been sealed in filling, protruded 1 cm. above the water in the bath, and a current of hot air was blown on to the tips to drive down any liquid into the body of the tube. The volumes of the phases were then read through a telescope 3 feet from the glass front of the thermostat, strong illumination being supplied through a ground glass screen behind the tubes. The mixing and manipulations were repeated until the readings were constant, the values in practice being reproducible to less than 0·01 c.c. The possibility of error due to the difference in shape of the ether–water and ether–air meniscuses was examined by a trial with pure paraffin (b. p. 60—70°) and water. Any error involved is less than that of observation.

A redetermination of the solubilities of ethyl ether at several temperatures gave the following results :

Temp.	Ether in aqueous phase.	Water in ether phase.
25°	6·03% (6·03)	1·30% (1·34)
20	6·87 (6·90)	1·24 (1·26)
15	7·95 (7·91)	1·26 (1·24)
10	9·01 (9·04)	1·14 (1·16)

The agreement with Hill's values (in brackets) is close, and there is reason to believe that the reduction of scale of the experiments has not introduced an error as large as 0·05%. Apart from this, our figures are presumably subject to a small error inherent in the original method when very low solubilities are measured (compare Kablukov and Malischeva, *J. Amer. Chem. Soc.*, 1925, **47**, 1553; Hill and Malisoff, *ibid.*, 1926, **48**, 918). This error is not large, and, being systematic, will not affect the validity of any comparison made between similar values of solubility. We obtained an indication of some error of this kind by comparing the figures for *n*-propyl ether, obtained by the method described above, with those found by the "synthetic" method of Alexejew (*Wied. Ann.*, 1886, **28**, 305). In this case the latter figures are consistently 0·2% lower than the former. For a few of the ethers examined, determinations were made by the synthetic method and for the aqueous phase only. Weighed quantities of the ether and of water were sealed up together, and the temperature at which turbidity just appeared was determined in a large vessel of water.

TABLE I.

A = weight % of ether in aqueous phase. B = weight % of water in ether phase.

Ether.		25°.	20°.	15°.	10°.	0°.
Methyl *n*-butyl	A	0·89	1·00	1·18	1·51	2·51
Q + 6800 cals.	B	0·91	0·71	0·57	0·45	0·50
Methyl *iso*butyl	A	1·10	1·24	1·51	1·79	2·53
Q + 6050 cals.	B	2·02	1·78	1·54	1·30	0·92
Methyl *sec.*-butyl	A	1·60	1·79	2·05	2·33	3·24
Q + 4350 cals.	B	1·95	1·69	1·48	1·22	0·80
Methyl *tert.*-butyl	A	5·16	5·83	6·55	7·30	9·12
Q + 3700 cals.	B	2·95	2·54	2·20	1·84	1·17
Ethyl *n*-propyl	A	1·87	2·03	2·32	2·74	3·66
Q + 4950 cals.	B	1·13	1·01	0·88	0·76	0·69
Ethyl *iso*propyl	A	2·40	2·82	3·35	3·99	5·89
Q + 5700 cals.	B	0·52	0·41	0·30	0·22	0·26
Diallyl	A	8·86	9·18	9·61	10·20	11·68
Q + 1750 cals.	B	1·51	1·25	1·05	0·91	0·71
Di-*n*-propyl	A	0·49	0·54	0·61	0·71	1·05
	B	0·45	0·38	0·31	0·29	0·36

TABLE II.

Weights % of ether in water.

Ether.	25°.	20°.	15°.	10°.	0°.
Di-*n*-propyl	0·25	0·30	0·38	0·41	0·58
n-Propyl *iso*propyl ...	0·47	0·51	0·60	0·75	—
Methyl *n*-propyl	3·05	3·2	3·4	3·8	5·6
Methyl *iso*propyl	6·5	7·4	8·6	9·7	—
Di-*n*-butyl	Solubility less than 0·01% at 17° (2 litres of water did not completely dissolve 0·2 g.).				

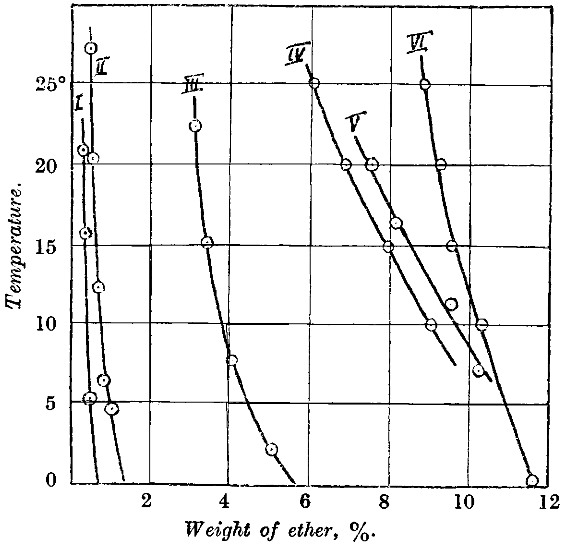
Results.—Measurements by the volumetric method were made at 25°, 20°, 15°, 10°, and 0·25° or 0·5°. Two separate sets of measurements were made in each case. The resulting data for the isomeric ethers $C_5H_{12}O$ are plotted in Fig. 2, the scale being doubled for the right-hand curves for the sake of clearness. The values recorded in Table I have been taken from the smooth curves : the corrections thus introduced are usually of the order ± 0—0·05%. The curves in Fig. 3, except those of ethyl and allyl ethers, record measurements by the synthetic method, and the smoothed values are given in Table II.

Discussion of Results.

The solubilities of water in the ethers are all small, and vary very little with temperature. Those of the ethers in water vary over a wide range for the isomeric substances studied. These values, moreover, all decrease with rising temperature. Approximate values of the (positive) molecular heats of solution (*Q*) of the ethers in water have been calculated in the usual way from the slopes of the solubility curves at 10—20° and are recorded in Table I.

It is noticeable that the relative order of the solubilities of the compounds remains the same at all temperatures. For the isomeric ethers $C_5H_{12}O$, this order is : Methyl *n*-butyl (1·51), methyl *iso*butyl (1·79), methyl *sec.*-butyl (2·33), ethyl *n*-propyl (2·74), ethyl *iso*propyl (3·99), methyl *tert.*-butyl (7·30), the figures in brackets being the values at 10°. The order for the isomerides $C_4H_{10}O$ is: Methyl *n*-propyl (3·8), diethyl (9·0), and methyl *iso*propyl (9·7). Throughout these values the solubility is seen to increase with increased branching of the carbon chains of the alkyl groups.

FIG. 3.



Solubilities in water of :

I. *Di-*n*-propyl ether.*
II. *Propyl* iso*propyl ether.*
III. *Methyl* n*-propyl ether.*
IV. *Diethyl ether.*
V. *Methyl* iso*propyl ether.*
VI. *Diallyl ether.*

The various physical properties of ethers in the pure state show them to be correctly classified as "normal" liquids. Evidence of various kinds is available in the case of ethyl ether : surface tension data are given by Morgan and Stone (*J. Amer. Chem. Soc.*, 1913, **35**, 1505) showing the same result with ethyl *n*-propyl ether, and measurements of the solubility of naphthalene in some of these ethers, which lead to the same conclusion, are recorded in Part II of this investigation; but the considerable solubility of the ethers in water indicates " abnormal " behaviour, and classifies them as " polar " in the sense suggested by G. N. Lewis (*ibid.*, p. 1448). This abnormality, absent in the pure liquid but developed in presence of water, is evidence of the presence in the latter case of a new molecular species of a polar type. Moreover, the comparative solubilities may be taken as an approximate indication of variations in the extent of the chemical action to form the complex $R_2O \longrightarrow HOH$. This point of view has recently been clearly stated by Sidgwick (Presidential Address to the British Association, Section B, 1927, and " The Electronic Theory of Valency," p. 137), who also explains the abnormally high solubilities in ether of hydroxylic substances in general as due to combination of the two to give the polar compound $R_2O \longrightarrow HOR$.

Three factors might consequently be expected to influence the solubilities in water of ethers which are of the same molecular weight.

(*a*) The chemical reactivity of the oxygen atom might be lowered by any accumulation of groups in its vicinity. Such a steric hindrance should cause a diminution in the solubility of isomerides as a normal radical is replaced by a secondary or tertiary one.

(*b*) The donating properties of the oxygen atom should, on the other hand, be increased if the attached radicals have an increased tendency to repel electrons (the " electron-source " effect). The experiments of Allan, Oxford, Robinson, and Smith (J., 1926, 401) have shown that the methyl group and particularly secondary alkyl radicals have this type of influence on a contiguous oxygen atom, as shown by its activity in controlling aromatic substitution. For this reason, therefore, the attachment of a secondary or tertiary radical to the oxygen of an ether should cause an increased solubility in water. An effect of this kind is somewhat similar to that which results in the higher strength of secondary aliphatic bases as compared with primary bases.

(*c*) Any increase in the length of a hydrocarbon chain will tend to reduce the solubility in water of the ether or of its complex with water (compare Langmuir, *Colloid Symposium Monograph*, Vol. 3, Chem. Catalog. Co., New York, 1925). It should be noticed that this effect is purely negative. The substitution of the *tert.*-butyl for the *n*-butyl radical does not, in the absence of an oxygen atom, confer an appreciable solubility on a substance, for *n*- and *iso*-butane are equally sparingly soluble in water.

The steric hindrance effect (*a*) appears to have been demonstrated for certain complexes of the alcohols by the experiments of Tschelinzeff (*Bull. Soc. chim.*, 1924, **35**, 741), but our figures do not reveal it. It is possible that this influence is present, but of a lower order of magnitude than the other effects, which oppose it. To the latter effects, (*b*) and (*c*), may be attributed the observed variations of solubility. Although in general these two influences cannot be observed separately, the increased solubility of $MeO{\cdot}CH_2{\cdot}CHMe_2$ as compared with $MeO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Me$ does presumably depend entirely on the length of hydrocarbon chain (*c*), whilst the increased value for $MeO{\cdot}CHMe{\cdot}CH_2Me$ as compared with $MeO{\cdot}CH_2{\cdot}CHMe_2$ reveals factor (*b*) independently of (*c*). The rapid fall in solubility with lengthened hydrocarbon chain, when molecular weight does not remain constant, is well shown by the following ethers : Ethyl (9·0), ethyl *n*-propyl (2·74), dipropyl (0·41), dibutyl ($<0{\cdot}01$). In the molecule of diallyl ether the unsaturated groups confer a considerable freedom of movement of electrons, which should assist the donating function of the oxygen atom. The relatively high solubility of this substance was therefore to be expected.

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