761. *The Solubility of Alkali Metals in Ethers.*

By J. L. Down, J. Lewis, B. Moore, and G. Wilkinson.

Potassium and sodium–potassium eutectic dissolve slightly (of the order of 10^{-4} g.-atom/l.) in certain ethers to give unstable blue solutions which are considered to be similar to the well-known blue solutions of alkali metals in ammonia and amines. Absorption spectra of the solutions show maxima at about 7000 Å.

An attempt has been made to correlate the ability to give a blue solution with the structure and basicity of the ethers.

It has previously been reported [1] that moderately stable blue solutions of potassium and sodium–potassium alloy in some ethers may be obtained. Solubility has since been observed in some fifteen ethers and one amino-ether. The solutions are immediately decolorised by air but they can be filtered through a sintered-glass disc *in vacuo*. Filtered solutions decolorise at room temperature, rapidly in some cases and slowly in others, owing principally to attack on the solvent by the alkali metal. The nature of the decomposition products has not been investigated. Generally, the total alkali-metal concentration appears to increase with decrease in temperature; in some ethers, *viz.*, the dimethyl ethers of polyethylene glycols, the surface of the sodium–potassium alloy exhibits a copper-coloured lustre at low temperature, presumably on account of the formation of alkali-metal

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[1] Down, Lewis, Moore, and Wilkinson, *Proc. Chem. Soc.*, 1957, 209 (where references to previous work with water and alcohols are given).

etherates, analogous to the copper-coloured ammoniates formed on evaporation of liquid ammonia solutions of alkali metals.[2]

RESULTS AND DISCUSSION

The extent of the solubility of potassium and sodium–potassium alloy in various ethers and amines as estimated visually from the intensities of the blue colorations is shown in Table 1; the dielectric constant and the basicity (as determined by O–D shifts) of certain ethers are also cited.

The only metals which have been found to give blue solutions are potassium and sodium–potassium alloy; at a given temperature the alloy solutions were always more intensely coloured than the solutions with potassium alone but this may possibly be a surface effect since the liquid alloy always presents a clean surface. Sodium is found in the blue solutions, however, but in view of the low total metal solubility ($\sim 10^{-4}$ g.-atom/l.) it is difficult to be certain that this may not be due to attack on the solvent either by the metal or by traces of oxides leading to the formation of soluble sodium salts such as alkoxides. It may be noted, however, that Ubbelohde[3] did not report a blue coloration when sodium was stimulated ultrasonically in ethylene glycol dimethyl ether; further, we have detected no sodium in a blue solution obtained from frozen sodium–potassium alloy.

Lithium, sodium, and calcium have failed to give blue solutions even in the most favourable ethers; since it is very difficult indeed to obtain clean surfaces of the metals, this result may not be conclusive, although in the case of sodium the experiment by Ubbelohde (noted above) strongly suggests that sodium is indeed insoluble in ethylene glycol dimethyl ether. Since some of the factors noted below, particularly the solvation effect, would have been expected to favour the solubility of the lighter alkali metals, it seems reasonable to attribute the failure to dissolve in the ethers, which are of course of rather low dielectric constant, to the higher ionisation potentials; we hence predict that rubidium and cæsium will give blue solutions, although the rate of attack on ethers may be high.

It seems reasonable to assume that, as in liquid ammonia and amines, the metal atoms dissolved in ethers are dissociated to give " solvated " electrons and solvated cations. The solubility will thus depend to a large extent on the ability of the solvent molecules to stabilise such species in solution.

The various factors which could influence the solubility properties of a given series of ethers are as follows: (1) The donor power of the oxygen atom; here, differences in the electron-donor ability are reflected in changes in the position of the O–D stretching frequency in the infrared spectra of solutions of $CH_3{\cdot}OD$ in the ethers.[4] (2) The dielectric constant of the ether. (3) The number of oxygen atoms in the ether. (4) The size of the ring formed in a chelated solvate of a cation. (5) Steric interaction by substituents near to the oxygen atom of the ether. (6) Stability of the solvent towards reduction by " solvated " electrons.

Certain of these factors are obviously inter-related. However, the major factors that appear to influence the solubility of the metal in ethers are (3), (4), and (5), and it seems that to a large extent the factors are those relating to solvation of the alkali-metal ion. Of course, the criteria for solvation of the electron, which would also provide a driving force for the solubility, are considerably more difficult to discern. Most of the ethers which give blue solutions contain more than one oxygen atom; co-ordination of the oxygen atom to a metal ion in solution would lead to the formation of five-membered chelate rings, and the solubility may be associated with this effect. It is well known that steric effects play an important part in complex formation generally; in the present case, the

[2] Ruff, *Ber.*, 1901, **34**, 2604.
[3] Slough and Ubbelohde, *Proc. Chem. Soc.*, 1957, 918.
[4] Gordy, *J. Chem. Phys.*, 1939, **7**, 93.

presence of bulky substituents near the oxygen atoms clearly decreases the ability of the ethers to dissolve metals, even though little or no change in the basicity of the ether is involved.

TABLE 1. *Solubilities of metals in various solvents.*

Solvent	Dielectric constant	O–D shift (cm.$^{-1}$)	Metal	Colour at room temp.
Dimethyl ether	7·4		Na–K	None
Diethyl ether	4·22	95	Na–K	None
Di-isopropyl ether		106	Na–K	None
Ethylene glycol ethers				
Dimethyl	5·50	92	Na–K	Intense
,,			K	Moderate
,,			Na	None
,,			Li	None
,,			Ca	None
,,			K/Hg	Blue surface on amalgam
,,			Na/Hg	None
,,			NaK/Hg	Blue surface on amalgam
Ethyl methyl		91	Na–K	Pale
Diethyl	5·10	88	Na–K	None
Methyl n-propyl		93	Na–K	None
n-Butyl methyl		92	Na–K	None
Diethylene glycol ethers				
Dimethyl	5·79	94	Na–K	Intense
Diethyl	5·70	91	Na–K	Pale
Ethyl methyl		93	Na–K	Moderate
Methyl n-propyl				Pale [a]
n-Butyl methyl	5·34	94	Na–K	Very pale [a]
Cyclic ethers				
Tetrahydropyran	5·44		Na–K	None
Tetrahydrofuran	6·00	112	Na–K	Pale
1-Methoxymethyltetrahydrofuran		106	Na–K	Intense
1-Ethoxymethyltetrahydrofuran		103		Moderate [b]
1-Propoxymethyltetrahydrofuran			Na–K	None
2-Methyltetrahydrofuran	4·63		Na–K	Very pale [a]
Dioxan	2·23		Na–K	None
Trimethylene oxide		114	Na–K	None
Cyclic tetramer of propylene oxide		114	Na–K	Intense
Miscellaneous				
1 : 2-Dimethoxypropane		94	Na–K	Very pale [a]
1 : 3-Dimethoxypropane	5·48	95	Na–K	None
2 : 3-Dimethoxybutane		96	Na–K	None
1 : 2 : 3-Trimethoxypropane		95	Na–K	None
Triethylene glycol dimethyl ether		95	Na–K	Very intense
Tetraethylene glycol dimethyl ether			Na–K	Very intense
Pentamethylene glycol dimethyl ether	5·27		Na–K	None
Amines				
Diethylamine	3·7		Na–K	None
Triethylamine	3·15		Na–K	None
Ethylenediamine	16·0		Na–K	Very intense
Methoxyethylamine			Na–K	Very intense

[a] Only on prolonged cooling to 193° K. [b] Pale at room temperature; moderate on cooling to 193° K.

(a) *Simple and cyclic monoethers.* The fact that no alkali-metal solutions have been obtained in dialkyl monoethers is probably due to steric hindrance in formation of a cation solvate as compared with cyclic monoethers. This comparison has been made in a different context by Ferguson.[5] No solubility was observed in tetrahydropyran and dioxan, where the oxygen atoms have lower electron-donor abilities than those in trimethylene oxide and tetrahydrofuran.[6]

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[5] Ferguson, *J. Amer. Chem. Soc.*, 1955, **77**, 5289.

[6] Searle and Tamres, *J. Amer. Chem. Soc.*, 1951, **73**, 3704.

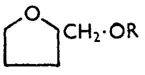
(b) *Ethylene glycol ethers,* $RO\cdot CH_2\cdot CH_2\cdot OR'$. When $R = R' = Me$, deep-blue solutions may be obtained, but replacement by $R = R' = Et$ results in no solubility, presumably owing to steric hindrance. The intermediate ether where $R = Me$, $R' = Et$, gives a solution of intermediate colour intensity. If $R = Me$ and $R' = Pr^n$ or Bu^n, no blue solution is obtained, indicating that one of the oxygen atoms is sufficiently " shielded " to prevent chelate-ring formation. Further evidence of steric inhibition is seen when the solubility is lowered as one, and then two, methyl groups are introduced into the $-CH_2\cdot CH_2-$ chain in ethylene glycol dimethyl ether.

(c) *Ethers of diethylene glycol,* $RO\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot OR'$. The ethers in this series will behave as tridentate ligands, giving rise to higher solubility than for the ethylene glycol ether when $R = R' = Me$. However, successive replacement of one of the terminal methyl groups by Pr^n, Bu^n lowers the tendency to dissolve. When $R = R' = Et$, the steric hindrance is not quite large enough to prevent slight solubility.

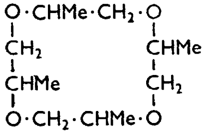
(d) $CH_3\cdot[O\cdot CH_2\cdot CH_2]_n\cdot O\cdot CH_3$. As n increases from 1 to 4 there is a very marked increase in solubility owing to an increase in the number of donor atoms per ether molecule. Entropy effects of chelation will evidently become more pronounced as n increases.

(e) $CH_3\cdot O\cdot[CH_2]_n\cdot O\cdot CH_3$. As would be expected, when $n > 2$, the chelate rings are unstable and no solubility is observed when $n = 3$ and 5.

(f) *Miscellaneous ethers.* Alkoxymethyltetrahydrofurans (I), which combine the low steric hindrance associated with the cyclic ether and the chelation effect due to the presence of a second oxygen atom, give blue solutions, solubility being greatest when $R = Me$ and gradually decreasing to zero when $R = Et$, Pr^n.



(I)



(II)

The cyclic tetramer of propylene oxide (II) gives a deep-blue solution of appreciable stability. Whilst the chelating possibility of this ether is obviously important, it may be noted that the high viscosity may be responsible in part for the stability of these solutions; the stability of filtered blue solutions in other ethers does indeed appear to be higher for the more viscous ethers.

(g) *Amines.* As would be expected from previous work by Birch,[7] no solubility was observed for diethylamine and triethylamine. This is to be expected since the ease of complex formation decreases in the order $NH_3 > RNH_2 > R_2NH > R_3N$, the last being almost devoid of ability to co-ordinate with metal ions. It seems that steric effects rather than differences in electron-donor ability are mainly responsible for this decrease, since tertiary amines co-ordinate firmly with the hydrogen ion. The observation that lithium does not dissolve in dimethylamine, although it is quite soluble in the isomeric ethylamine, is further evidence of the importance of steric effects in the solubility property towards alkali metals.

It is noteworthy that 2-methoxyethylamine gives intensely coloured solutions.

Absorption Spectra.—The absorption spectra of blue solutions of potassium and sodium–potassium alloy in some ethers (Table 2) were measured in the wavelength region 22,000—6000 Å; all spectra showed only a well-defined maximum at about 7000 Å. The positions of the maxima did not alter with changes in temperature or concentration. The spectrum of potassium in ethylene glycol dimethyl ether showed a small shoulder at 8290 Å.

Solutions of alkali metals in ammonia and amines show one or both of two very intense absorption bands—one in the visible (~6500 Å) and the other in the infrared (~15,000 Å) region. Solutions showing the former are diamagnetic while those showing the latter are

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[7] Birch and MacDonald, " Oxford Science," 1948, **1**.

paramagnetic. It has been suggested[8,9] that in such solutions, paired and unpaired "solvated" electrons, respectively, exist in cavities. At the same time it has been observed that in solutions showing both absorption bands, there is evidence to indicate that an equilibrium exists between the two electronic species.

For solutions of alkali metals in ethers, no bands were observed in the region 13,000—18,000 Å, which corresponds to the e_1 type cavities in ammonia and amine solutions. Such solutions would therefore be expected to be diamagnetic. Although we observed no paramagnetic resonance signals from a frozen blue solution of sodium–potassium alloy in ethylene glycol dimethyl ether at temperatures down to 90° K, Weissman[10] reports a weak spin resonance absorption line, about 2 œrsteds in breadth, from a solution of potassium in the same solvent at 193° K.

TABLE 2. *Absorption spectra of blue solutions in ethers.*

Ether	Metal	$\lambda_{\text{max.}}$ (Å)
Ethylene glycol dimethyl ether	Na–K	7075
,, ,,	K	7290, 8290 (sh)
Tetrahydrofuran	Na–K	7050
1-Methoxymethyltetrahydrofuran	Na–K	7150
,, ,, ,,	K	7170
Diethylene glycol dimethyl ether	Na–K	6990
2-Methoxyethylamine	Na–K	7170
,, ,,	K	6800

Solubility Measurements.—Attempts have been made to determine the solubilities of potassium and sodium–potassium alloy in ethylene glycol dimethyl ether, and also that of this alloy in tetrahydrofuran, 1-methoxymethyltetrahydrofuran and diethylene glycol dimethyl ether. Initially, the determinations were made by measuring the alkali-metal content by using a flame photometer. The solubility is in all cases very low and we cannot consider the measurements reliable since the total alkali content possibly included unknown contributions arising from soluble decomposition products of the ether and from oxides in the metals. Hence a few solubilities were determined by measuring the volume of hydrogen evolved when a blue solution was decomposed by water.

We conclude that the maximum upper limit of the solubilities is of the order of 10^{-4} g.-atom/l. for each alkali metal. There is some evidence to suggest that potassium has a negative, and sodium a positive, temperature coefficient of solubility. This is in agreement with the solubilities of these metals in ammonia. Furthermore, the solubility of potassium alone in ethylene glycol dimethyl ether appears to show a shallow minimum at about —30° C. The attack on the ether would increase with temperature, and the general shape of the curve of the apparent solubility of potassium in ethylene glycol dimethyl ether could arise from a concomitant increasing decomposition and decreasing solubility with temperature.

EXPERIMENTAL

As the solutions were unstable to air they were handled *in vacuo* or in oxygen-free nitrogen, methods similar to those described previously[8] being used.

Preparation and Purification of Materials.—*Solvents.* Several ethers were available commercially. Others were prepared from available hydroxy-compounds by the Williamson method. The products were fractionally distilled, freed from alcohols by refluxing them over sodium, and distilled from lithium aluminium hydride in a stream of nitrogen.

The cyclic tetramer of propylene oxide was prepared by polymerisation with boron trifluoride–ether complex, according to a method kindly provided by Mr. W. J. Toussaint of Union Carbide Chemicals Co., which is as follows: Dry propylene oxide (2198 g.) was added to a flask equipped with a stirrer, a brine-cooled condenser, and a feed tank for catalyst addition. The

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[8] Fowles, McGregor, and Symons, *J.*, 1957, 665, 3329.

[9] Ogg, *J. Chem. Phys.*, 1946, **14**, 114.

[10] Weissman, *J. Amer. Chem. Soc.*, 1958, **80**, 5342.

propylene oxide was heated under reflux while being stirred. The catalyst [boron trifluoride–ethyl ether complex (47% BF_3, 56 g.)] was fed in during 7 hr. at such a rate as to maintain vigorous boiling without application of external heat. The crude product was boiled for 2 hr., the final flask temperature being 68°. Unchanged propylene oxide and ethyl ether were removed by distillation to a head temperature of 33° at 180 mm., to a flask temperature of 80°. The boron trifluoride in the crude product was neutralised by stirring and heating it at 85° for 2 hr. with sodium hydroxide solution (75 g. in 500 ml. of water). The lower layer was removed while hot. The product was washed twice at 85° with 250-ml. portions of water, the heated lower layer being removed each time. The remaining water was removed by distillation up to 75° at 34 mm. with a flask temperature of 120°. The tetramer was separated from low- and higher-boiling fractions by distillation through a 1″ × 18″ column of stainless-steel protruded packing. The fractions boiling at 94—122°/5 mm. were collected, combined, and redistilled (yield 38%). The main tetramer fraction was taken at 104·8—105·5°/5 mm.

Amines were dried by refluxing them over potassium hydroxide pellets and then over sodium.

Metals. Since lithium cannot be distilled *in vacuo* in glass apparatus, samples were cut from the centre of a large piece under light petroleum and transferred to the apparatus against a stream of nitrogen. Sodium and potassium were cut from the centre of large pieces under light petroleum and inserted into the apparatus against a stream of nitrogen. The metals were then melted, degassed, and distilled *in vacuo.*

The sodium–potassium eutectic (75% potassium w/w) was transferred in nitrogen, degassed by heating *in vacuo*, and filtered through a plug of glass wool.

Preparation of Blue Solutions.—The solvents were distilled *in vacuo* in a previously degassed apparatus. Solvents were condensed on to sodium and potassium, but in the case of sodium–potassium alloy this was added to the solvents by rotating the bulb containing it around a ground-glass joint. The sample bulb, containing alkali metal and solvent, was then sealed off, and the blue solution obtained by shaking and cooling as necessary.

Measurement of Absorption Spectra.—The absorption spectra were measured *in vacuo* in a 1-cm. fused silica cell fitted with a graded silica-to-Pyrex seal, a Perkin-Elmer Model 4000 recording spectrophotometer being used. The pure solvent was used as the reference liquid. The blue solutions were filtered through a sintered disc into the cell, which was placed in a conventional Dewar system for work at low temperatures.

Solubilities.—The apparatus used to generate blue solutions was immersed in a large Dewar vessel, containing a suitable refrigerant. The solutions were kept in the bath for a standard time of 30 min., being removed periodically and shaken vigorously; they were then filtered through a sintered disc into a bulb. The filtrate was weighed and evaporated to dryness, and the residue made up to 100 ml. with 1% sulphuric acid. The alkali content was determined with an EEL flame photometer calibrated with standard sodium and potassium sulphate solutions in 1% sulphuric acid.

For the determination of the hydrogen evolved, the solvent was degassed *in situ* by melting and freezing it at least ten times. The pressure was measured before and after condensation of degassed water on to the filtrate, frozen at 77° K, by a McLeod gauge.

The following solubilities (in g.-atoms/l. × 10^4) were found. (*a*) By the hydrogen method at 0° in ethylene glycol dimethyl ether, 1 (K), 4 (Na–K); in tetrahydrofuran, 2 (Na–K); these values were the mean of four determinations, the spread being about 2. (*b*) By the flame photometer method: for K in ethylene glycol dimethyl ether: 23°, 4; 0°, 2; −23°, 1; −35°, 2; −48°, 2; −65°, 4; for Na–K in ethyl glycol dimethyl ether: 20°, 4 (Na), 5 (K); 10°, 8 (Na), 10 (K); 0°, 8 (Na), 6 (K); −13°, 8 (Na), 5 (K); −23°, 13 (Na), 3 (K); for Na–K in tetrahydrofuran: 0°, 6 (Na), 3 (K); for Na–K in 1-methoxymethyltetrahydrofuran: 21°, 8 (Na), 2 (K); for Na–K in diethylene glycol dimethyl ether: 21°, 100 (Na), 160 (K).

Dielectric Constants.—These were determined in the standard manner, benzene being used as a reference.

O–D *Shifts.*—These were determined by Gordy's method.[4] $CH_3{\cdot}OD$ was prepared by the hydrolysis of magnesium methoxide with deuterium oxide. The positions of the O–D peaks in the infrared spectra of approximately M-solutions of $CH_3{\cdot}OD$ in the ethers were measured by using a Perkin-Elmer Model 21C recording infrared spectrophotometer, equipped with calcium fluoride optics. A 0·1M-solution of $CH_3{\cdot}OD$ in carbon tetrachloride was taken as a reference. The O–D peak in the reference solution occurred at 2691 cm.$^{-1}$, the spectrum being calibrated by means of the carbon dioxide peak at 2350 cm.$^{-1}$.

Preparative Use of Sodium–Potassium Alloy in Ethylene Glycol Dimethyl Ether.—Solutions of this alloy may be used in preparative chemistry. The alloy is injected into a three-necked flask containing ethylene glycol dimethyl ether under a nitrogen atmosphere. If a blue solution is not formed immediately, cooling in carbon dioxide–acetone produces the required solution. Reactions which are normally carried out by using sodium shot or sodium amalgam in ethers or other inert solvents, usually take place more rapidly in the alloy–ether medium.

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INORGANIC CHEMISTRY RESEARCH LABORATORIES,
IMPERIAL COLLEGE, LONDON, S.W.7.

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