Physcio-chemical studies on the systems uranyl nitrate – organic solvent - water

Mathieson A. R.,

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PHYSICO-CHEMICAL STUDIES ON THE SYSTEMS URANYL NITRATE - ORGANIC SOLVENT - WATER

A.R. Mathieson, B.Sc.(Dunelm), A.R.I.C.

Thesis presented for the degree of M.Sc. in Pure Science

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The experimental work described in this thesis was performed at the Atomic Energy Research Establishment, Harwell, during the period November 1947 - December 1949.

The results have already been published elsewhere:

Mathieson "Stability of Complexes of Uranyl Nitrate with Ketones and Ethers", J. Chem. Soc., 1949, S 294.

McKay and Mathieson "The Partition of Uranyl Nitrate between Water and Organic Solvents, Part I" Trans. Farad. Soc., 1951, 47, 428.

Glueckauf, McKay and Mathieson "The Partition of Uranyl Nitrate between Water and Organic Solvents, Part II" Trans. Farad. Soc., 1951, 47, 437.

A report on a related topic will also be found in Glueckauf, McKay and Mathieson "The activity coefficient of Uranyl Nitrate in the presence of Sodium Nitrate" J. Chem. Soc., 1949, S 299.

The thanks of the authors are due to the Director of the Atomic Energy Research Establishment for permission to publish the work.

The author wishes to place on record his best thanks to H.A.C. McKay, Esq., who supervised the work, and to Dr. E. Glueckauf under whose direction the work was carried out.

Index to Chapters

I. Previous Work on the Interaction of Uranyl Nitrate with Solvents

I. In common with certain other metallic nitrates, such as those of Nickel, Cobalt, Magnesium and Thorium, Uranyl Nitrate is soluble in organic solvents. It differs from them, however, both in the magnitude of its solubility and in the much larger range of solvents in which it is soluble. The solubility of a highly ionised salt[1] in so large a range of non-polar liquids is unusual, and warrants investigation both for its own sake and because of the light it may shed upon the general problem of solubility relations.

It has been long known that uranyl nitrate was soluble in several organic solvents. Peligot[2] and Sir Wm. Crookes[3] found that it dissolved in methyl and ethyl ethers, Naumann and Alexander[4], and Naumann, Rill and Bezold[5] that it dissolved in methyl and ethyl acetates, Moore and B. and H. Schbindt[6] that it dissolved in ethyl acetoacetate, Naumann and Schroeder[7] that it dissolved in pyridine, and de Coninck[8] that it dissolved in acetone, formic and acetic acids, methyl and ethyl acetates, and acetic anhydride. Finally, Yaffé[9] made a comprehensive survey of solvents. He measured the solubility of uranyl nitrate hexahydrate in the solvents at 25°C, and discovered that it is insoluble in hydrocarbons, but soluble in almost any oxygenated organic solvent. Although he stated that the solubility of uranyl nitrate hexahydrate in the solvents falls off with increasing complexity of the organic molecule, and that addition of an ether, carbonyl, hydroxyl, or carboxyl group to the solvent greatly enhances solubility, he failed to discover any direct relation between the solubility of uranyl nitrate in, and the oxygen content of, the solvent. That such a relationship does exist is shown in section V.

The literature contains the records of some work on solutions of uranyl nitrate in diethyl ether, and of more on the hydrates of uranyl nitrate, but most of it is old (cirea 1910) and some of it conflicting. Misciatelli[10] and Guempel[11] made independent phase studies of the system uranyl nitrate - diethyl ether - water. They recognise only two solid phases, $UO_2(NO_3)_2.6H_2O$ and $UO_2(NO_3)_2$, at ordinary temperatures, but they are in disagreement over the properties of anhydrous uranyl nitrate. Marketos[12] claimed to have prepared anhydrous uranyl nitrate by passing a current of CO_2 and HNO_3 vapour over uranyl nitrate hexahydrate at 170-180°C, and von Unruth[13] by drying an ethereal solution of uranyl nitrate trihydrate with $CaCl_2$, metallic sodium, or anhydrous $CuSO_4$. Späth[14] and de Forcrand[15] give other methods of preparation, but the authors are in disagreement over the products of the different methods. This conflicting evidence throws the preparation of anhydrous unco-ordinated uranyl nitrate into considerable doubt and renders unacceptable the work of Misciatelli and Guempel without further evidence. Before the work described in this thesis was completed, Katzin and Sullivan[16] published a further investigation on the lines of those of Misciatelli and Guempel, and found no evidence of the existence of unco-ordinated uranyl nitrate. Their results are discussed in greater detail in section II.

Hydrates of uranyl nitrate having 6, 3 and 2 molecules of water per molecule of salt are well established[17]. De Coninck[8] claimed to have prepared one having 4 molecules of water by keeping uranyl nitrate hexahydrate crystals at 100°C for a few hours, but Lescoeur[18] found that the hexahydrate decomposes at 85°C losing water and nitric acid. That the latter observation is the true one can be verified very simply. Katzin and Sullivan[16] claim a tetrahydrate however.

Uranyl salts are known to form many complexes with organic molecules[19,20,21,22,23]. Uranyl nitrate will also form complex compounds with some of its solvents, such complexes having been reported by von Unruth[13], who claimed to have prepared, by evaporation in dry air or in vacuo of the ethereal layer of a solution of uranyl nitrate hexahydrate in diethyl ether, a complex $UO_2(NO_3)_2 \cdot 3H_2O \cdot (C_2H_5)_2O$, and a further complex $UO_2(NO_3)_2 \cdot 2(C_2H_5)_2O$ from a solution of uranyl nitrate trihydrate in ether. From the system uranyl nitrate - ammonia - ether he claimed to have isolated four complexes, $UO_2(NO_3)_2 \cdot 2NH_3$, $UO_2(NO_3)_2 \cdot 2NH_3 \cdot (C_2H_5)_2O$, $UO_2(NO_3)_2 \cdot 4NH_3$, and $UO_2(NO_3)_2 \cdot 3NH_3 \cdot (C_2H_5)_2O$. Chantrel[24] has also prepared a number of organic complexes of uranyl nitrate including one with dioxane, and he considers it possible that hydrogen bonding might give rise to such organic complexes.

II. In 1949, Katzin and Sullivan published two papers on the interaction of uranyl nitrate and organic solvents. The first paper[25] described the analysis of twelve organic solvates of uranyl nitrate, thus establishing that the phenomenon is general. The second[16] contained the results of an investigation of the system uranyl nitrate - organic solvent - water by the well-known Schreinemakers rest-method.

The first paper gives the following results of the analysis of the solvates (UN represents $UO_2(NO_3)_2$ and S represents the solvent).

/over

Results from AECD 2213

Solvent	Composition of Solvate	Type of Solvate
Diethyl ether	$UN.2{\cdot}03H_2O.4{\cdot}39S$	Hexasolvate with trapped ether
Diethyl ether	$UN.2.53H_2O.0{\cdot}97S$	Tetrasolvate with ether lost
Diethyl ethylene glycol	$UN.1{\cdot}97H_2O.1.89S$	Tetrasolvate
Diethyl diethylene glycol	$UN.2{\cdot}21H_2O.2{\cdot}07S$	Tetrasolvate
Dibutyl diethylene glycol	$UN.2{\cdot}08H_2O.2{\cdot}16S$	Tetrasolvate
Acetone	$UN.2{\cdot}00H_2O.0{\cdot}94S$	Trisolvate
Methyl propyl ketone	$UN.2{\cdot}43H_2O.0{\cdot}41S$	Trisolvate
Methyl isobutyl ketone	$UN.2{\cdot}71H_2O.0{\cdot}28S$	Trisolvate
Di-isopropyl ketone	$UN.0{\cdot}29H_2O.1{\cdot}91S$	Disolvate
Ethyl acetate	$UN.0{\cdot}87H_2O.1{\cdot}34S$	Disolvate
Ethyl propionate	$UN.2{\cdot}72H_2O.0{\cdot}24S$	Trisolvate
Isobutyl alcohol	$UN.0.41H_2O.2{\cdot}52S$	Trisolvate

Table 1.

The phenomenon is evidently general, and the complexes are usually tetra-, tri-, or di-solvated. Tetrasolvation can occur in the presence of organic solvent, whereas with water as solvate this is apparently impossible.

The second paper gives the results of the investigations of the system uranyl nitrate - organic solvent - water, for the solvents diethyl ether, β-ethoxyethyl ether, dihexyl ether, acetone, methyl isobutyl ketone, and isobutyl and tertiary butyl alcohols. It is noteworthy that the solvents used were commercial products not further purified, and experience shows that they probably contained large quantities of impurity. The experimental details given are somewhat sparse, but the fact that water contents have been determined directly by the Karl Fischer method[26] represents a considerable advance. In each case, as the water content of the solutions was reduced, they found equilibrium solid phases having different compositions. Table 2 gives a list of the components of the solid phases in order of appearance. Never more than two can be present at once. The detailed results show that some components may have remained undetected. The solvate $UO_2(NO_3)_2.4H_2O$ formed in acetone solutions was never isolated from the other hydrates, so its existence was not finally established.

Components of Solid Phases

Solvent	Solvates
Diethyl ether	$UN.6H_2O$ $UN.3H_2O.S$ $UN.2H_2O.2S$ $UN.2S$
Dihexyl ether	$UN.6H_2O$ $UN.3H_2O$ $UN.2H_2O.2S$
Isobutyl alcohol	$UN.6H_2O$ $UN.3H_2O$ $UN.2H_2O.S$ $UN.2S$
Tertiary butyl alcohol	$UN.6H_2O$ $UN.3H_2O.3s$ $UN.2H_2O.4S$ $UN.3S$
β-ethoxyethyl ether	$UN.6H_2O$ $UN.3H_2O.S$ $UN.2H_2O.2S$
Acetone	$UN.6H_2O$ $UN.4H_2O$ $UN.3H_2O$ $UN.2H_2O.S$ $UN.2S$
Methyl isobutyl ketone	$UN.6H_2O$ $UN.3H_2O$ $UN.2H_2O.S$ $UN.2S$

Table 2.

Most of the solvates are tetra-, tri-, or di-solvates, but tertiary butyl alcohol shows some new hexasolvates. No uncoordinated uranyl nitrate was discovered. The solvate $UN.3H_2O.S$ for acetone described in section VI was either missed, or confused with the $UN.2H_2O.S$ given, as it was never isolated from other components.

For the water-saturated organic uranyl nitrate solutions, graphs of water concentration plotted against uranyl nitrate concentration (in molalities) give straight lines right up to saturation. This indicates that a definite number of water molecules are associated with a uranyl nitrate molecule, and from the slopes of the lines the numbers can be shown to be 4 for diethyl ether, β-ethoxyethyl ether in concentrated solution, methyl isobutyl ketone and isobutyl alcohol, 6 for β-ethoxyethyl ether in dilute solution, and 2 for dihexyl ether. (This research produced similar results prior to the publication of this paper). The figure 2 for dihexyl ether depends on one experimental point only. The solutions furthermore are very unstable, so that this particular result can probably be disregarded. The solubility of water in isobutyl alcohol given differs remarkably from established values[29], and results obtained in this research make these data suspect also (see section II). The initial line of slope 6 for β-ethoxyethyl ether, on examination of the detailed results, appears to be an S-shaped curve, and in this research a more probable curve for this solvent was obtained (Section II). However, the fact that 4 molecules of water are associated with each uranyl nitrate molecule in water-saturated solutions of some organic solvents does seem established. The partition curves of uranyl nitrate between water and methyl isobutyl ketone, diethyl ether, β-ethoxyethyl ether and isobutyl alcohol are also given.

In the light of these results, Katzin and Sullivan presented a theory of the solution of uranyl nitrate in organic solvents, based on a UO_2^{++} ion with a co-ordination number of 6, co-ordinating water and solvent up to this number in organic solution. Unfortunately they overlooked the possibility of the solutions being non-conducting and they did not investigate this. Section III shows that this is, in fact, the case, and so there can be little or no UO_2^{++} present in the solutions. Their theoretical conclusions can therefore be disregarded.

A complete description of the system uranyl nitrate - water - organic solvent would involve a detailed thermodynamic study of the partition equilibria of uranyl nitrate between water and organic solvents, a study of the phase diagrams of the systems, and a study of the solid solvates formed. The phase diagrams had already been obtained for several systems by Katzin and Sullivan, and so this research is mainly concerned with a study of the partition equilibria and the properties of the solutions.

To investigate the possibility of ionisation of the uranyl nitrate in organic solution, the conductivities, viscosities, and boiling points of these solutions were investigated. The water content of water-saturated solutions of uranyl nitrate in organic solvents was investigated for different uranyl nitrate concentrations to investigate further the hydration discovered by Katzin and Sullivan. The partition equilibria of uranyl nitrate between water and organic solvents were investigated, and a short study of the vapour pressures of aqueous uranyl nitrate solutions was made to investigate the possibility of ionic association or the existence of undissociated molecules in aqueous solution. In addition, a study of the stability of several of the solid solvates was made in an attempt to estimate the strength of the solvent co-ordination. Finally an attempt has been made to devise a theory which will explain adequately the results obtained.

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Chapter II. The Water Content of Organic Uranyl Nitrate Solutions

An investigation of the water content of water-saturated solutions of uranyl nitrate in organic solvents was undertaken by Katzin and Sullivan[1,2]. Their results indicated that, in many cases, each molecule of uranyl nitrate is associated with four molecules of water in organic solution. This section, which was undertaken before the publication of their results, confirms most of their conclusions but differs from them in certain significant details.

Since the experimental techniques used in this section of the investigation are relatively simple, they will be described first.

Experimental Section

Materials. All the materials used in the research will be described in this section.

1) The Uranyl Nitrate Hexahydrate used was of Analar quality, not further purified except when it was used to measure the vapour pressure of aqueous uranyl nitrate solutions, when it was recrystallised.

2) The water used was always glass-distilled.

3) The following organic solvents were purified by distillation, and drying by the appropriate methods:-
methyl ethyl ketone, diethyl ketone, isoamyl alcohol, sec-octyl alcohol, methyl isobutyl ketone, cyclohexanone, isobutyl alcohol, isoamyl acetate, di-isopropyl ether, diethyl ether.

4) The following solvents were purified by distillation, drying and treatment with $KMnO_4$ and NaOH to remove peroxides:-

dibutyl ether, β-butoxyethyl butyl ether, ββ' dibutoxyethyl ether, ββ' dibutoxyethoxyethyl ether, β-ethoxyethyl ether.

5) The sodium chloride and potassium chloride used were of Analar quality, not further purified.

Nomenclature. At this stage a note on the nomenclature and abbreviations to be used in the discussions is appropriate. Mono-ethers, ketones, alcohols, and esters will be denoted by their usual names. The ether $C_2H_5.O.C_2H_4.O.C_2H_5$ will be referred to as β-ethoxyethyl ether; C_4H_9 O C_2H_4 O C_4H_9 as β-butoxyethyl butyl ether; C_4H_9 O C_2H_4 O C_2H_4 O C_4H_9 as ββ' dibutoxyethyl ether; $C_4H_9.O.C_2H_4$ O C_2H_4 O C_2H_4 O C_2H_4 O C_4H_9 as ββ' dibutoxyethoxyethyl ether. The symbol 'UNH' will refer to $UO_2(NO_3)_2.6H_2O$; 'UNT' to $UO_2(NO_3)_2.3H_2O$; 'UN' to $UO_2(NO_3)_2$; 'UN x H_2O y S' to $UO_2(NO_3)_2$.x H_2O.y (solvent).

Techniques. In order to determine the amount of water present in a water-saturated solution of uranyl nitrate in an organic solvent, four different procedures are possible, each appropriate only to certain conditions. These are:

(i) The Karl Fischer method[3], involving direct volumetric estimation of the water, and analysis for uranium content by one of the usual methods. This method was used by Katzin and Sullivan[2], but was rejected in this research in favour of methods (ii), (iii) and (iv), which are considerably easier and quicker.

(ii) Titration of the organic uranyl nitrate solutions with water.
Crystals of $UO_2(NO_3)_2.6H_2O$ were dissolved in the solvent, and water was added from a burette until a permanent cloudiness appeared. The total water present was then

that added in titration plus that from the crystals. The weight of crystals used and the total volume of the solution give the $UO_2(NO_3)_2$ concentration. This method can only be used when the particular solution under investigation dissolves more water than that provided by the crystals of $UO_2(NO_3)_2.6H_2O$. It lead to experimental difficulties when the density of the organic uranyl nitrate solution and the aqueous solution in equilibrium with it were close together, because the aqueous phase became suspended in the form of small drops and was difficult to detect. The method was not used in such cases. $UO_2(NO_3)_2.6H_2O$ crystals were found, by uranium analysis, to contain always quite accurately the correct proportion of water.

(iii) The Phase Volume method

This method was applicable when the solution under investigation would dissolve less water than that added in the UNH crystals. UNH crystals were dissolved in the solvent, and a small aqueous phase formed. The solutions were well mixed to ensure that equilibrium was attained, and then centrifuged. The volume of the aqueous phase was then measured with a micropipette, and that of the organic phase with a burette. To calculate the concentrations of water and uranyl nitrate in the two phases, a knowledge of the partition coefficient of uranyl nitrate between water and the solvent, and of the densities of aqueous uranyl nitrate solutions is required. These were measured with sufficient accuracy by reweighing 10 mls. of solution, and the partitions were measured as described in Chapter V).

Let c = volume of aqueous phase, d = volume of organic phase, e = moles UNH/ml. in the aqueous phase, f = moles UNH/ml. in organic phase, b = total moles UNH, g = density of aqueous phase, p = weight of solvent in organic phase. Sussessive approximations of e and f are made until

$$(c \times e) + (d \times f) = b$$

Then the molality of H_2O in the organic phase is

$$\frac{\left[\frac{108b}{502}\right] - \left[cg - 394ce\right]}{^{18p}/_{1000}}$$

and the molality of uranyl nitrate in the organic phase = 1000fd. A small additional correction was sometimes necessary to allow for solvent dissolving in the aqueous phase. This procedure is much quicker than estimating the H_2O and UN in the organic phase by chemical analysis.

(iv) <u>The method of mixing</u>

This involves mixing two water-saturated organic uranyl nitrate solutions of different UN concentrations. According to the conditions, the resultant mixture will be water-saturated, rather less than saturated, or contain more water than the saturation quantity. Fig. I shows three possible curves of molality of water against molality of uranyl nitrate in water-saturated organic solution.

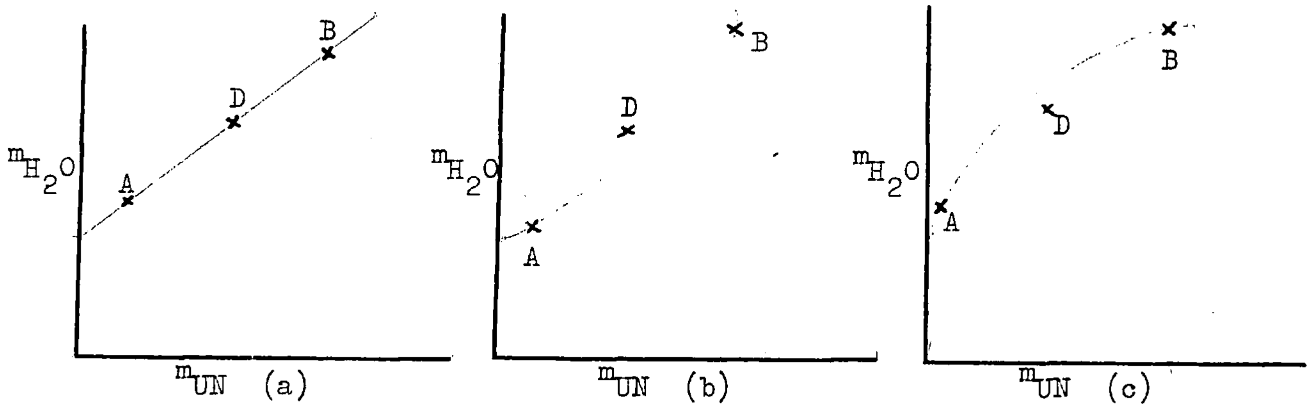

Fig. I

Mixing equal volumes of solutions A and B will result in solution D. If the plot is linear (Fig. Ia), D will be water-saturated. If the plot is concave (Fig. Ib) D will have too much water, and an aqueous phase will separate. The experiment is then treated as in method (iii). If the plot is convex (Fig. Ic), D will not be water-saturated, and the experiment is treated as in method (i). These mixing experiments will not only give more points on the m_{H_2O}/m_{UN} curves, but also afford a very sensitive test of the linearity of such a curve as Fig. Ia.

In practice only the last three methods were used because of their simplicity, and a comparison of the results obtained by these methods with those of Katzin and Sullivan using the Karl Fischer technique showed the simpler methods to be just as accurate. The results are shown in Figs. II - XIII and in tabular form in appendix I.

In many instances agreement is good between the figures presented here and those of Katzin and Sullivan. In a number of instances there are discrepancies, and in these cases the new results are probably to be preferred, since carefully purified solvents were employed, whereas Katzin and Sullivan employed "commercially pure" solvents only.

The first point on each curve represents the solubility of water in the organic solvent. In those cases where this quantity was already well established, these results agree well with the established value, except in the case of methyl ethyl ketone, where the determined solubility is 8.34 m. against a well-established value of 6.10 m. It must therefore be concluded that the purification of this solvent was inadequate, though it was established that it contained no alcohol or acetone. In a number of cases the solubility determinations are new, but since no great precautions were taken to ensure complete saturation, no priority is claimed for the figures.

The results for the different solvents are probably best discussed systematically, considering each class of solvent in turn.

1. Ethers (figs. II - VI)

In general the ethers gave linear plots having a slope of 4 - they obeyed the relation

$$m_{H_2O} = 4m_{UN} + \text{const.}$$

However there was some deviation from this general behaviour. Thus the curves for β-ethoxyethyl ether and $\beta\beta'$ dibutoxyethoxyethyl ether turn over at the highest values of m_{UN}, (fig. VI) and a slight deviation from linearity was established for $\beta\beta'$ dibutoxyethyl ether by the method of mixing over the range of $m_{UN} = 0.2 - 0.5$ (fig. V). The slope of 4 was found in all cases except that of β-ethoxyethyl ether, which gave a slope of 5.5 up to $m_{UN} = 2$, and turned over beyond that point.

These results indicate that, in general, a molecule of uranyl nitrate is associated with 4 molecules of water in ethereal solutions. Why the hydration figure should be greater in β-ethoxyethyl ether than in all the other ethers is not clear, but in this connection it may be pointed out that, if the hydrates are solvated also, the relative stability of different hydrates may depend on the solvating agent to some extent.

Katzin and Sullivan state that dihexyl ether also shows exceptional behaviour, giving a degree of hydration of 2. Careful experiments performed by Mr. T.V. Healy using peroxide-free dihexyl ether show however that a saturated solution of uranyl nitrate hexahydrate in the ether corresponds to the normal degree of hydration of 4.0.

The departure from linearity in the range $m_{UN} = 0.2 - 0.5$ for

$\beta\beta'$ dibutoxyethyl ether was discovered by chance. The low values which were obtained by the normal techniques, were quite reproducible. If the solutions were shaken for several hours the water content of the organic phase increased to the 'linear' value. This was the only case of this behaviour discovered in the ethers.

2. Esters

Isoamyl acetate was the only ester tested (fig. VII). It gave a linear plot, with a slope of 3.4.

3. Alcohols (figs. VIII - X)

The three alcohols tested all showed similar behaviour which differed from the behaviour of the other solvents. The curves showed an initial fall, indicating that the addition of uranyl nitrate up to $m_{UN} = 0.1 - 0.2$ actually decreases the solubility of water in the alcohols. Mixing experiments demonstrated the reality of the effect, and indeed examination of Katzin and Sullivan's[2] results shows that they observed the effect also but apparently ascribed it to experimental error. In this connection it is worth noticing that the figure given here for the solubility of water in isobutyl alcohol (11.5 m.) is much closer to the accepted value (11.2 m.) than is that of Katzin and Sullivan (9.8 m.)[2].

Low results were obtained for isoamyl alcohol, which were nevertheless reproducible, unless several hours equilibration were employed. This is analogous to the behaviour of $\beta\beta'$ dibutoxyethyl ether. It seems probable that the curve corresponding to complete equilibrium has not been obtained in the case of isoamyl alcohol.

After the initial fall, the alcohol curves rise, the upper portions being roughly linear. It is evident that the behaviour of the alcohols is a good deal more complex than that of the other solvents. The hydration values are generally less than 4, which suggests that alcohol molecules, by virtue of their hydroxyl groups, can replace water in the hydration shell. It is possible to give a tentative explanation of the initial fall of the curves as follows. If we subscribe to the view that the solubility of water in the alcohols is due in part to the formation of hydrogen bonds, it may be asserted that the uranyl nitrate molecules compete with water to become hydrogen bonded to the alcohol, thus reducing the solubility of water in the alcohol. This will explain adequately the initial fall in the curves. To explain the subsequent rise it may be imagined that this effect is competing with the normal hydration effect, which at greater uranyl nitrate concentrations becomes the dominant process. Such an explanation is of course tentative only and qualitative. To put it on a quantitative basis would require a great deal of further work.

4. Ketones (figs. XI - XIII)

Methyl isobutyl ketone and cyclohexanone showed normal linear plots of slope 4 (figs. XII and XIII), but methyl ethyl ketone (fig. XI) gave a plot of slope 5.3, actually increasing at high values of m_{UN}. The amount of water which can be carried into this solvent is enormous. At high values of m_{UN} there are more water than ketone molecules in the ketone phase. It would appear possible therefore that a point might be reached where the composition of the ketone phase becomes the same as the water phase. This was not borne out in practice however. Nevertheless, in view of the high water concentration, anomalous behaviour in this solvent is not surprising.

Summarising the results, it has been shown that uranyl nitrate is present, on the average, as a tetrahydrate in solution in the following solvents:- all ethers but β-ethoxyethyl ether, methyl isobutyl ketone, cyclohexanone. The hydration figures for other solvents are: isoamyl acetate 3.4, methyl ethyl ketone 5.3, β-ethoxyethyl ether 5.5. The alcohols show more complex behaviour.

Comparison with the results of Katzin and Sullivan[2] is possible in several cases. Their curves for diethyl ether and methyl isobutyl ketone are precisely similar to those presented here. For β-ethoxyethyl ether they interpret their results as two intersecting straight lines of slopes 6 and 4, but the curve is equally well interpreted as a smooth curve similar to that given here. The case of isobutyl alcohol has already been discussed.

<u>References to Chapter II.</u>

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3. Fischer, Angew.Chem. 1935, <u>48</u>, 394-396.

FIG. II. DIETHYL ETHER SOLUTIONS.

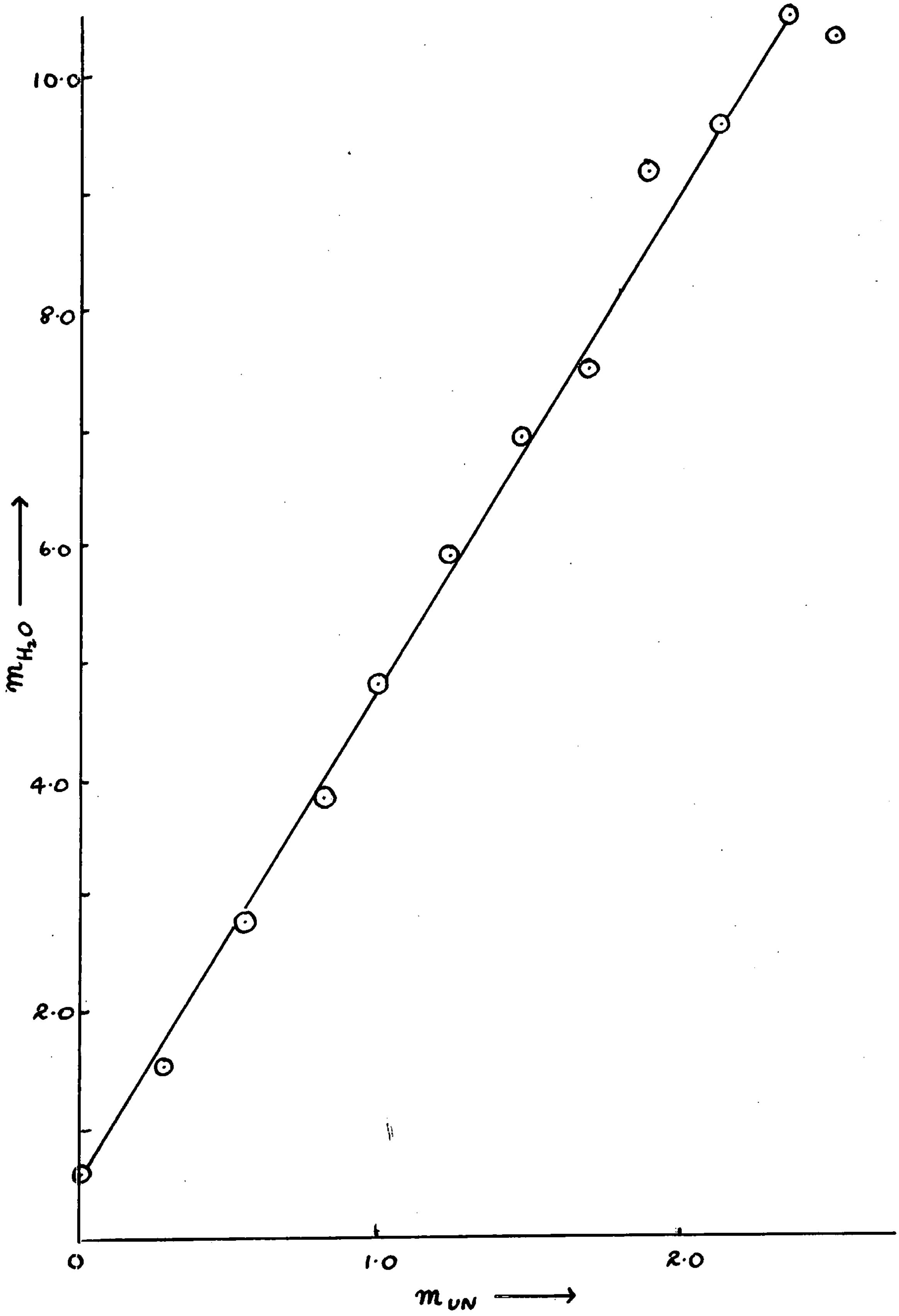


FIG. III. DI-ISOPROPYL ETHER

SOLUTIONS.

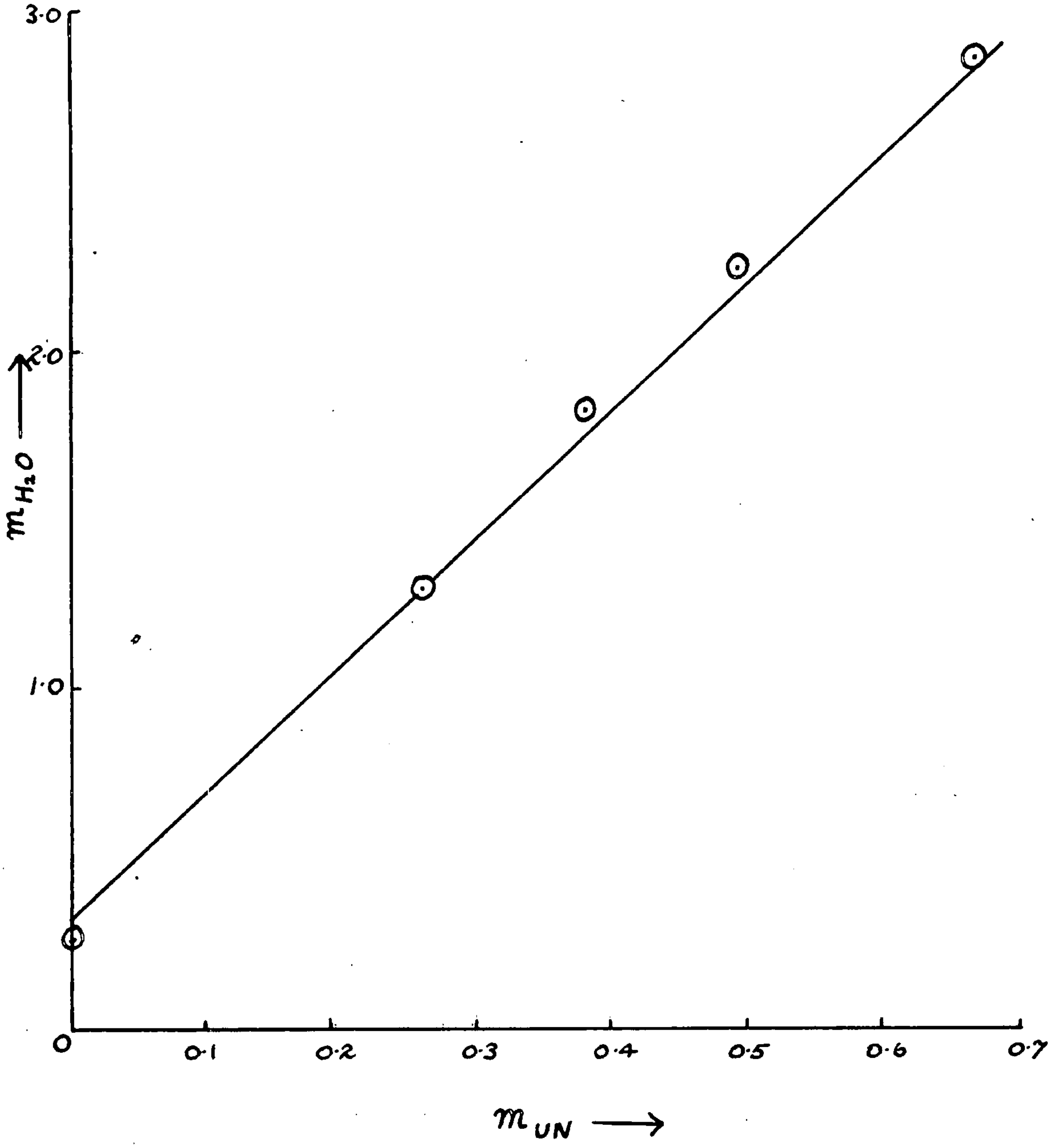


FIG. IV. DIBUTYL ETHER SOLUTIONS.

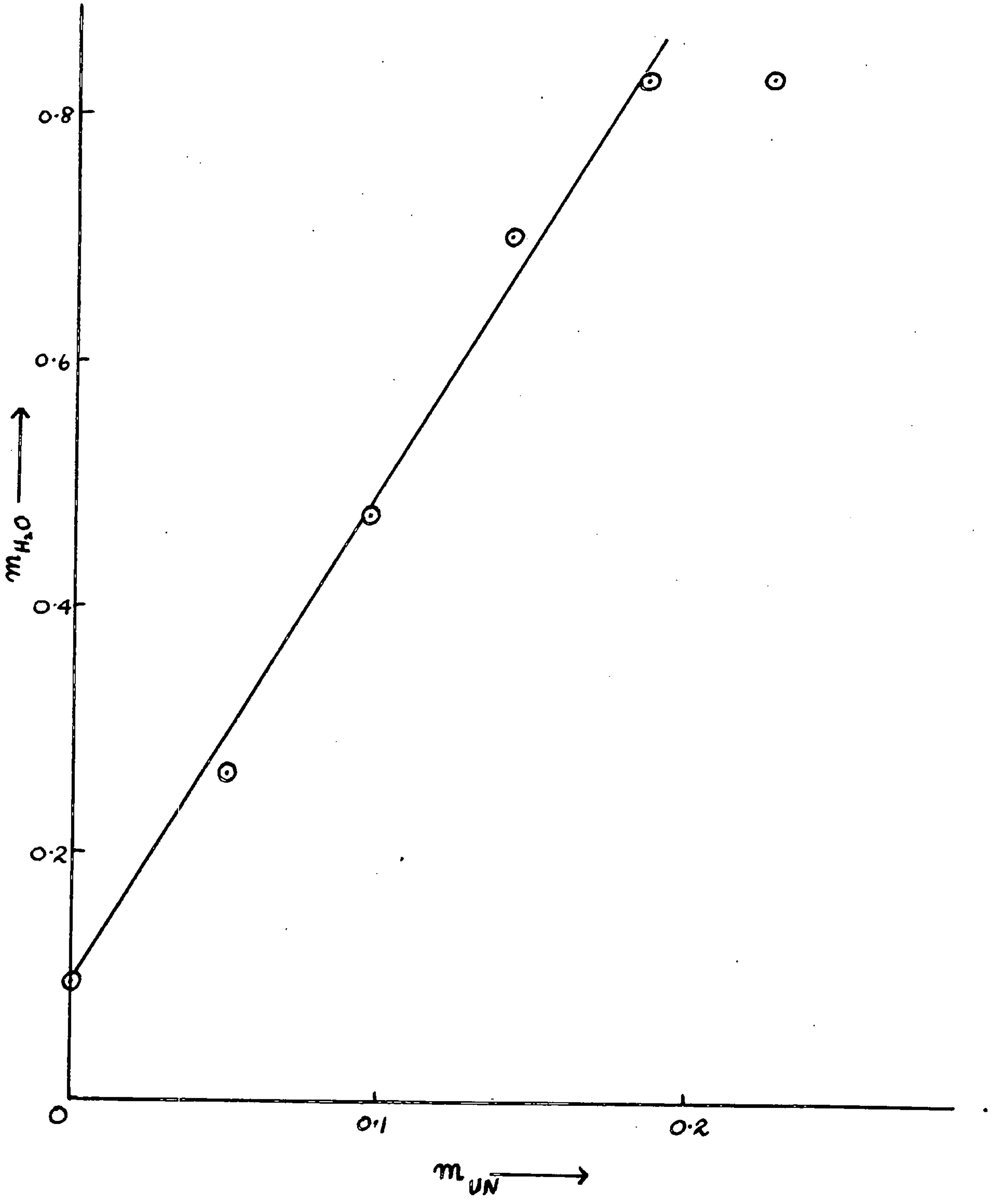


FIG.V. $\beta\beta'$-DIBUTOXYETHYL ETHER SOLUTIONS.

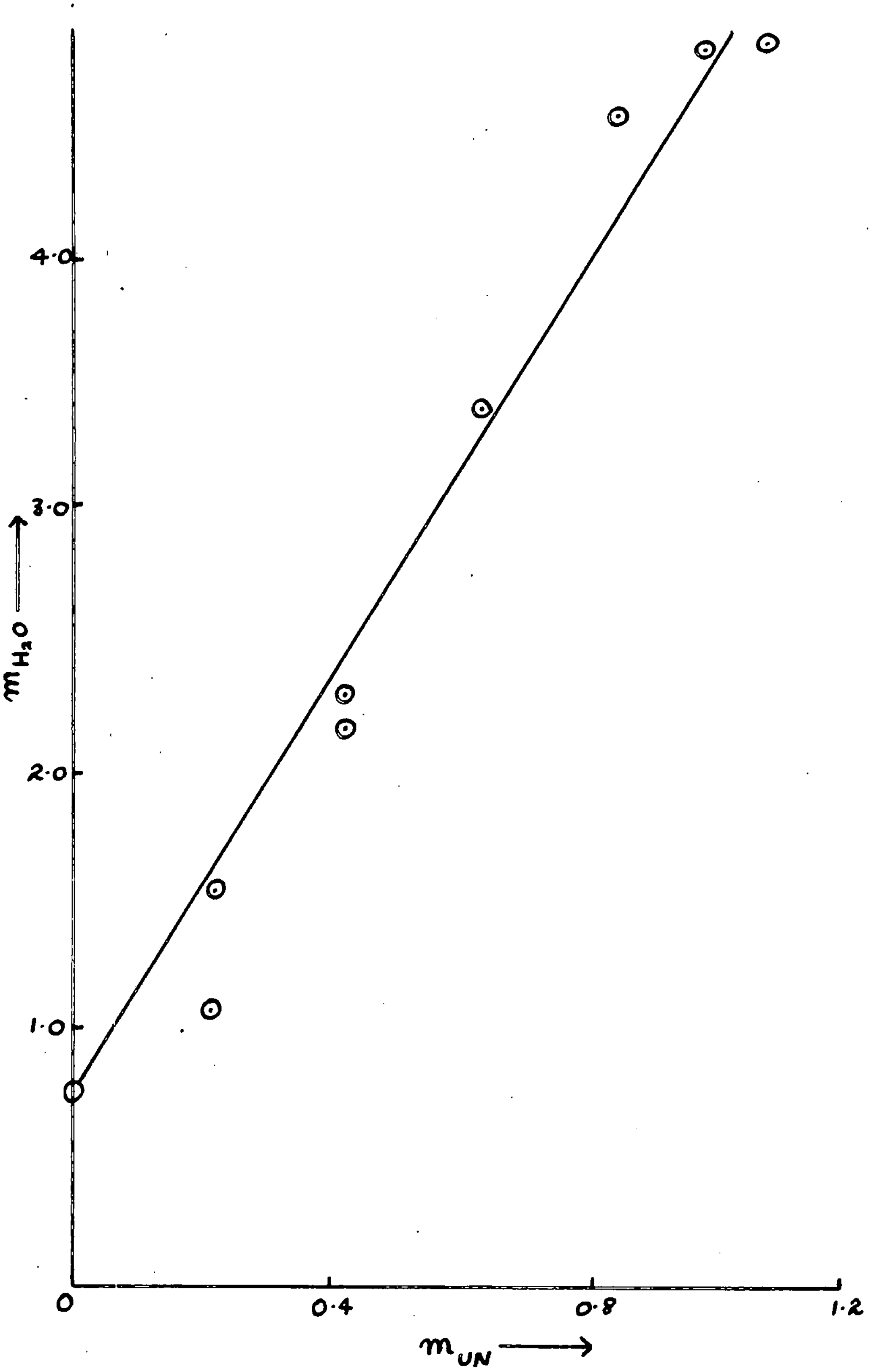


FIG. VI. (I) - β-ETHOXYETHYL ETHER SOLUTIONS.
(II) - ββ'-DIBUTOXYETHOXYETHYL ETHER SOLUTIONS.

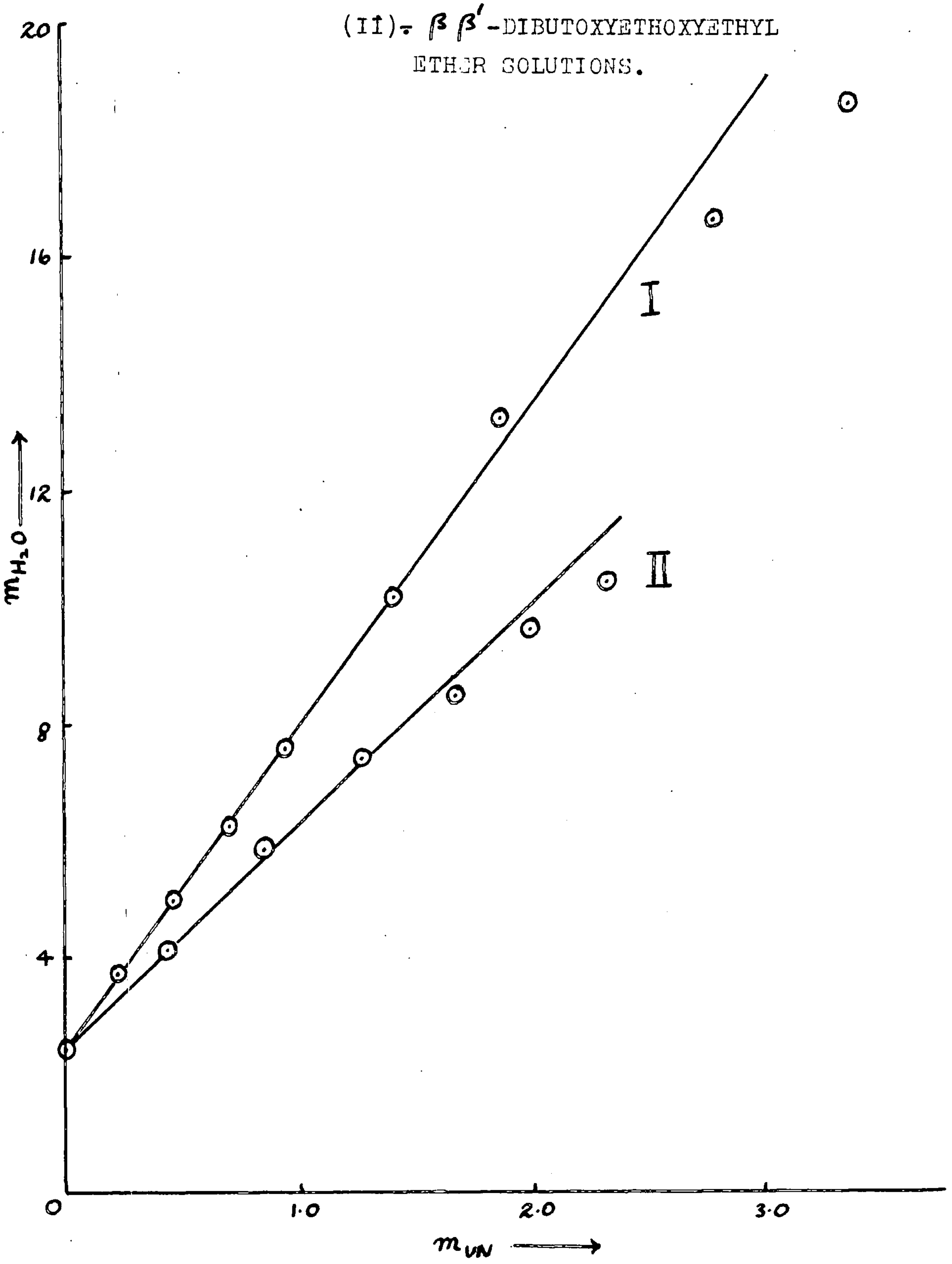


FIG. VII. ISOAMYL ACETATE SOLUTIONS.

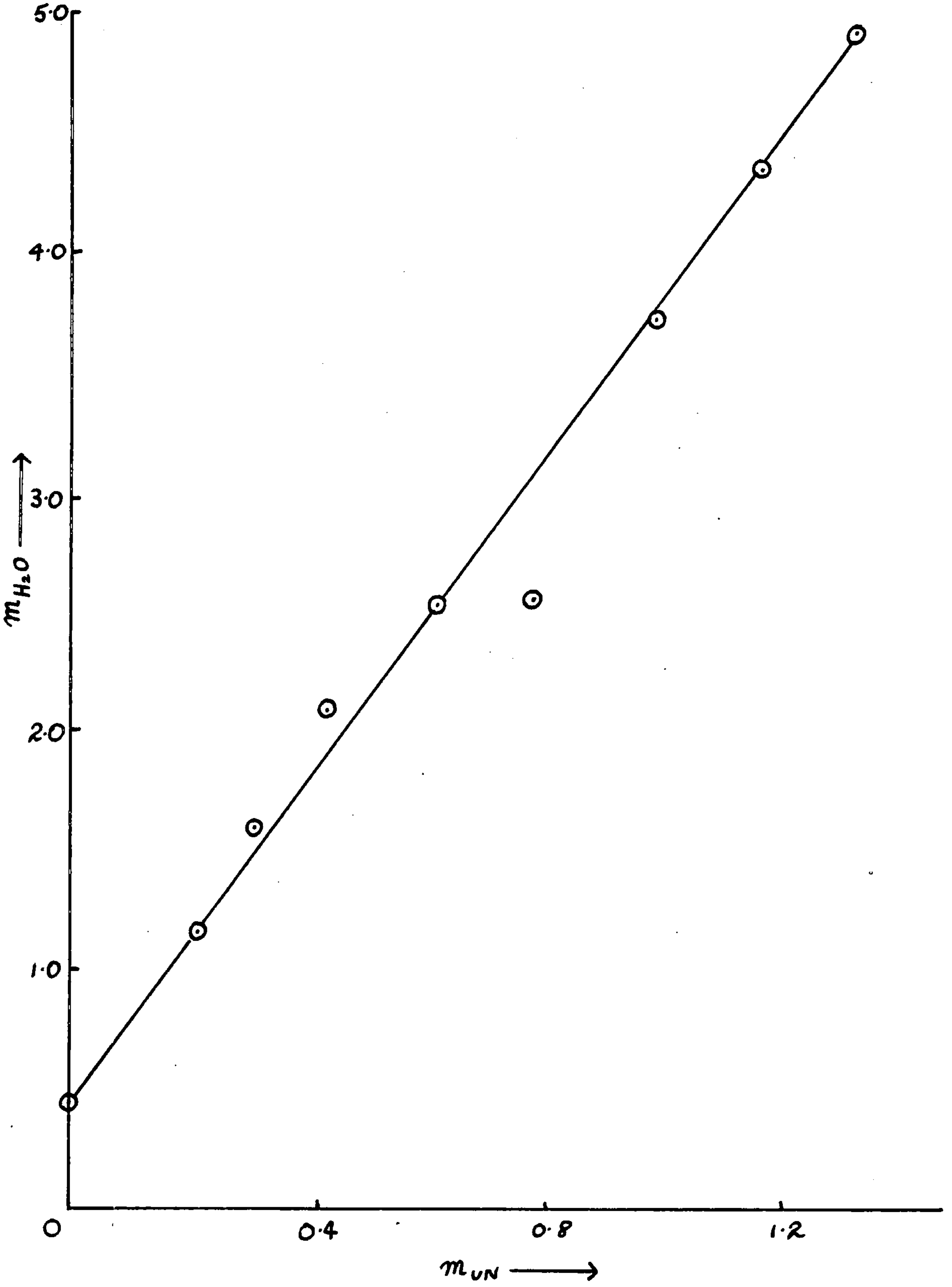


FIG.VIII. ISOBUTYL ALCOHOL SOLUTIONS.

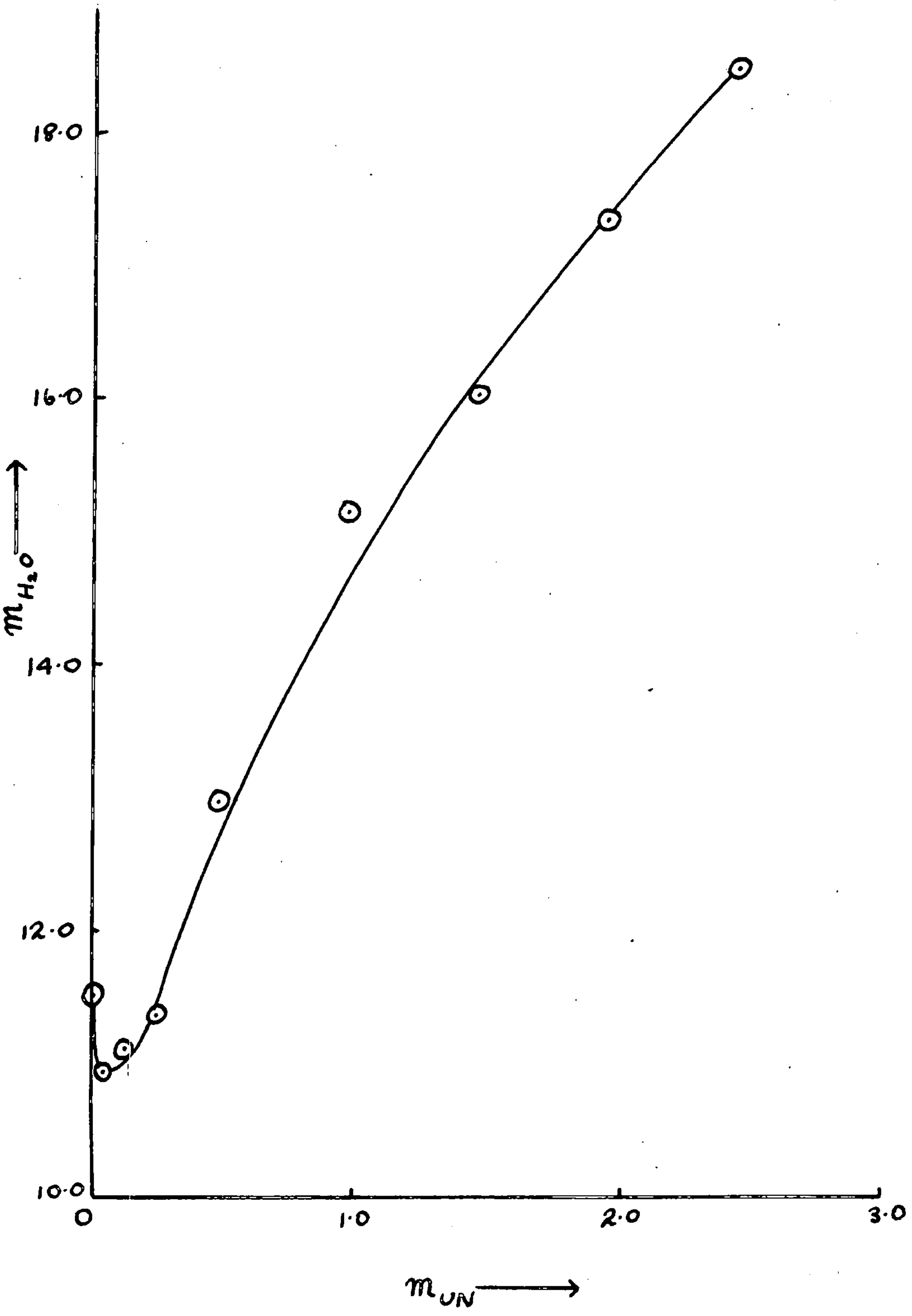


FIG. IX. ISOAMYL ALCOHOL SOLUTIONS.

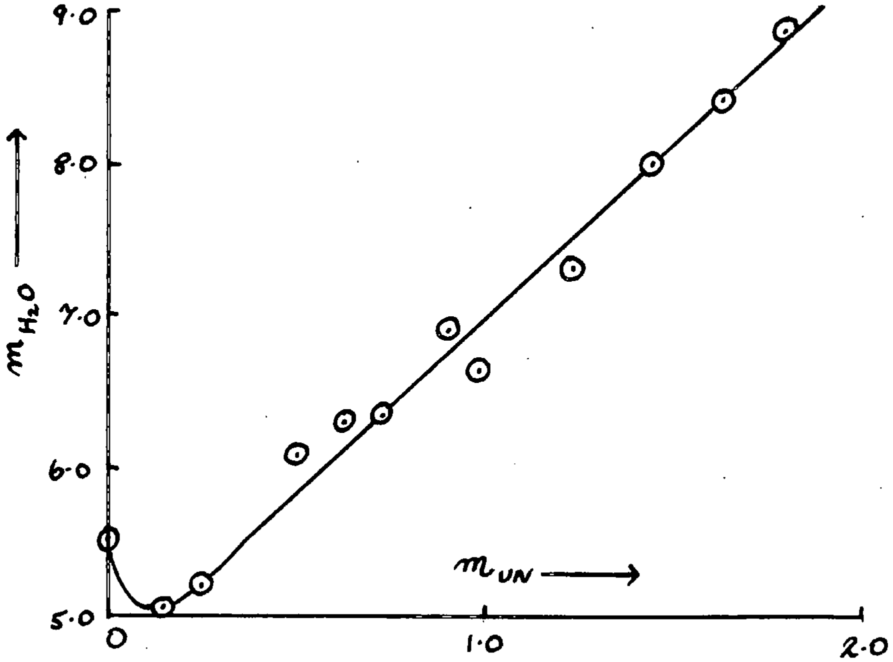


FIG.X. SEC-OCTYL ALCOHOL SOLUTIONS.

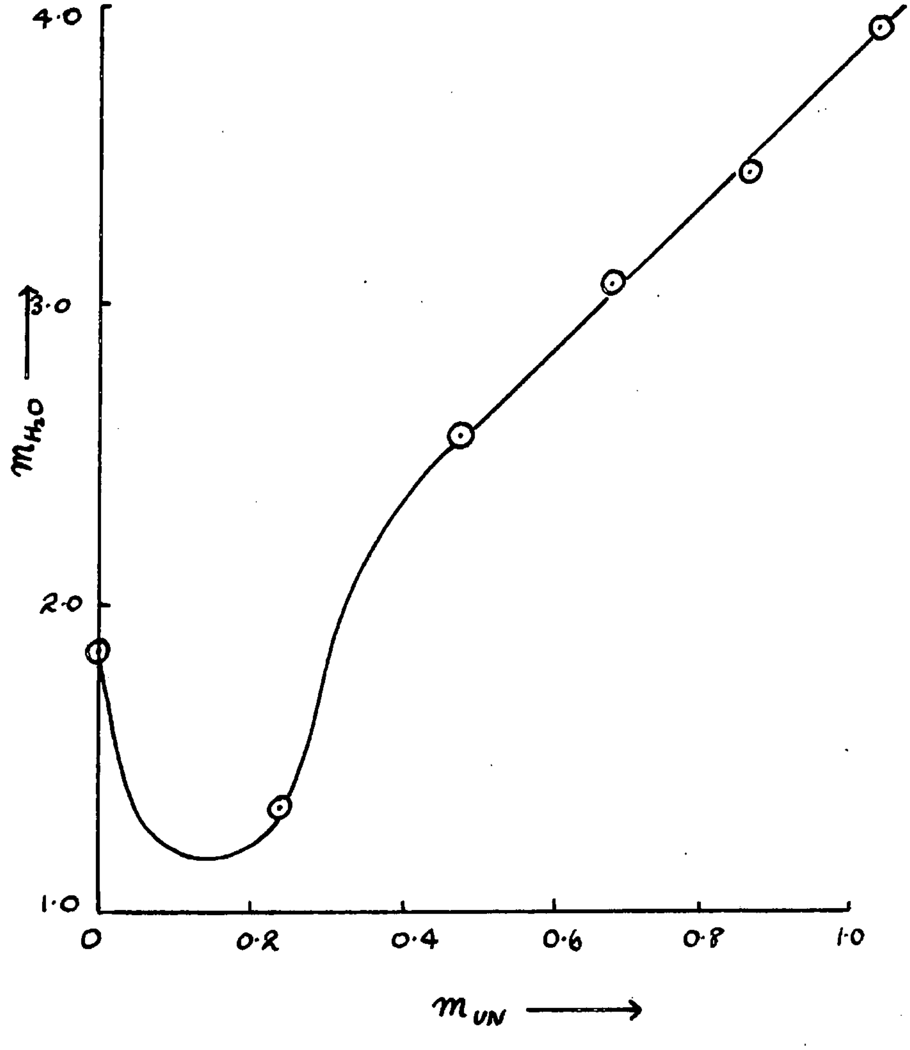


FIG.XI. METHYL ETHYL KETONE SOLUTIONS.

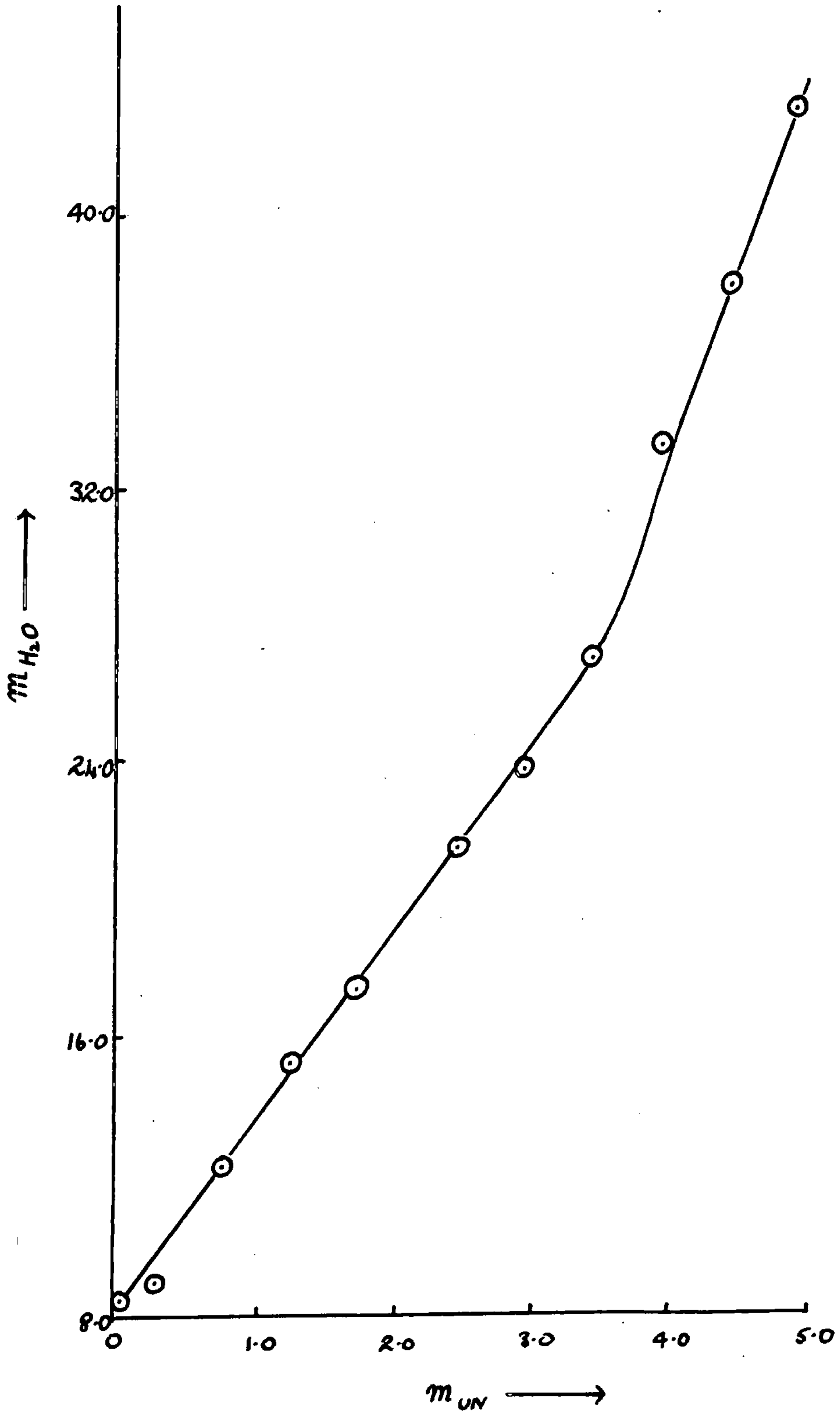


FIG. XII. METHYL ISOBUTYL KETONE SOLUTIONS.

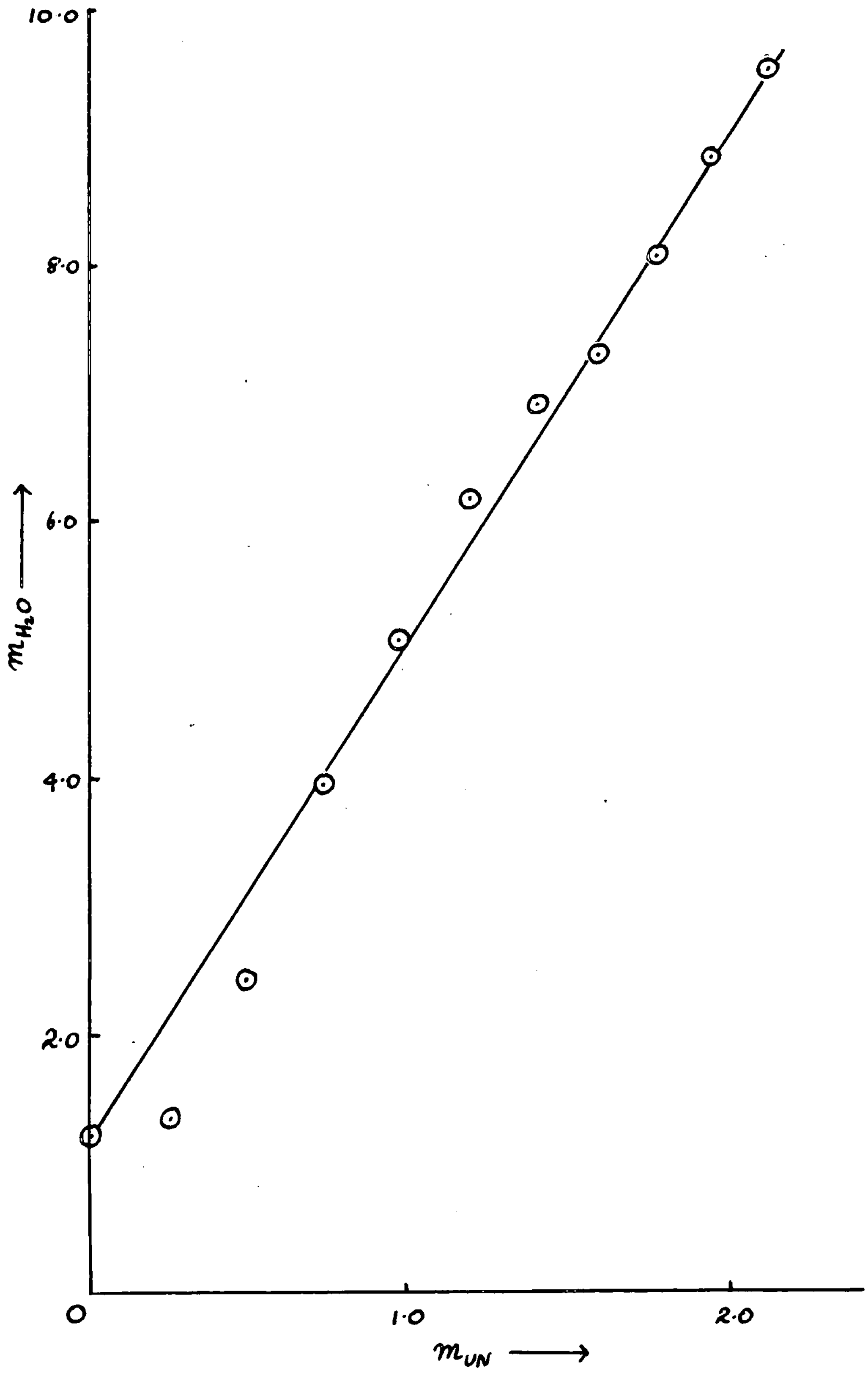
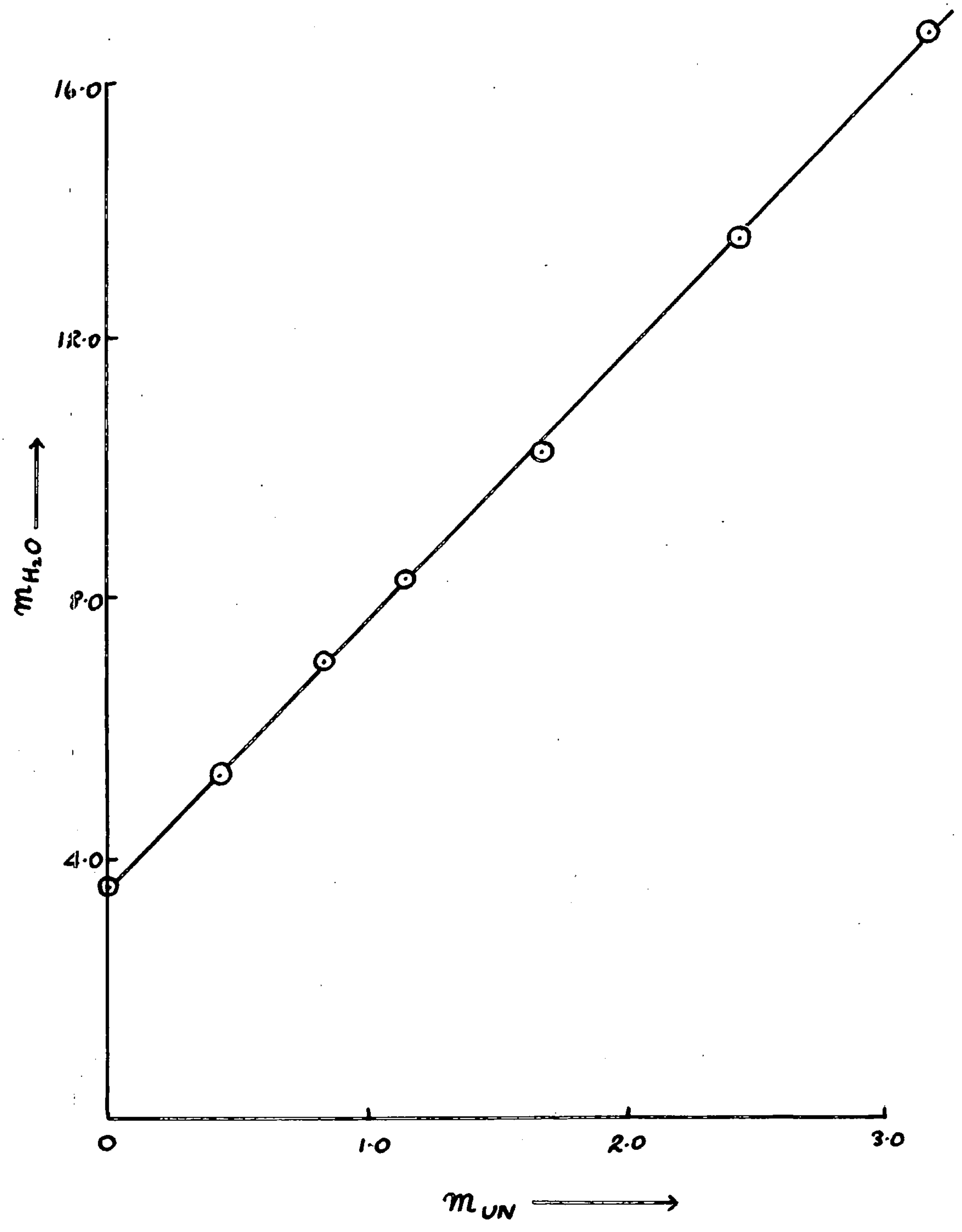


FIG. XIII. CYCLOHEXANONE SOLUTIONS.



Chapter III. The degree of ionisation in the organic phase

Having shown that 4 molecules of water are associated with each molecule of uranyl nitrate in organic solution, it was necessary to investigate the degree of ionisation of the solutions. Katzin and Sullivan[1] had based their speculations on the assumption that the organic solutions were ionized, but offered no evidence in support of this. The discovery of unionised $UO_2(NO_3)_2$ molecules in aqueous solution (Chapter IV) makes it more probable that the organic solutions are at least partly unionised. Two types of simple measurement can be made which will yield the necessary information:-

(i) Freezing or boiling point determinations
(ii) Conductivity measurements

Freezing point determinations are impractical because the solvents freeze at low temperatures, and the solutions generally decompose with boiling. Solutions in diethyl ether, however, boil without decomposition, so measurements were made on these solutions. Conductivities could be measured very simply, and when correlated with viscosity determinations, gave a measure of the degree of ionisation of the solutions.

Boiling points of diethyl ether solutions

The apparatus, which is shown in Fig. XIV, was of the Swietoslowski[2] design. The solution in bulb A is heated electrically at the top of the bulb, and a froth of liquid and vapour rises up tube B and squirts over the glass finger C, which contains a Beckmann thermometer with its bulb surrounded by mercury. Round the outside of the finger is wound a glass rod, and the chamber containing the finger is inside a vacuum flask. Tubes for the return of the liquid and the condensed vapour contain a drop counter which was used to ensure a constant rate of boiling.

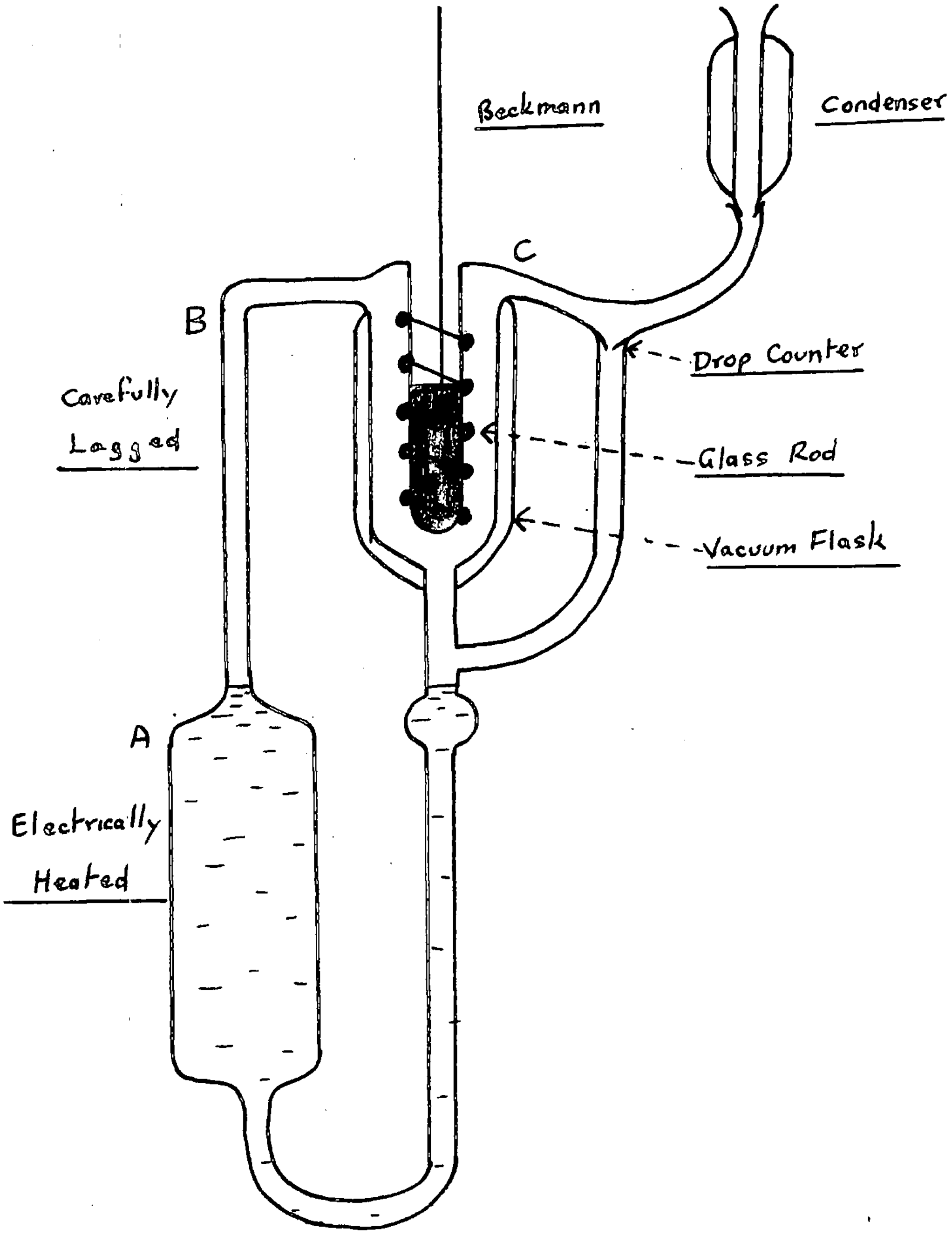

Beckmann
Condenser
C
B
Carefully Lagged
Drop Counter
Glass Rod
Vacuum Flask
A
Electrically Heated

Fig. XIV

A graph of drop rate as measured at the drop counter against boiling point appears as in Fig. XV. The drop rate was adjusted to the point A, which represented a rate of about one drop per second, and a steady reading was obtained for the boiling point. The disadvantages of the apparatus are

(i) it is not corrected for variation of atmospheric pressure

(ii) no account is taken of the quantity of pure solvent, vaporised from the solution, which exists in the upper tubes.

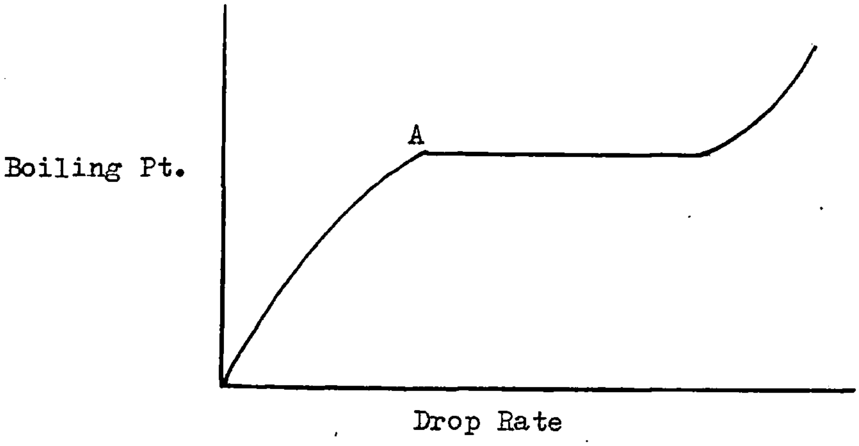


Fig. XV

It was, however, considered accurate enough to give the information required.

Two sets of solutions were examined.

(i) solutions of $UO_2(NO_3)_2.3H_2O$ in ether

(ii) solutions obtained by equilibrating ether with aqueous uranyl nitrate solutions. These would contain $UO_2(NO_3)_2.4H_2O$ plus that amount of water which the pure solvent dissolves.

The results are shown in tables 3 and 4, together with the boiling point elevations to be expected if only one solute species existed in the solution. Figs. XVI and XVII show plots of boiling point elevation against the mole ratio $^{\text{ether}}/\text{uranyl nitrate}$, the continuous line in each case representing the theoretical curve for one solute species, and the points the experimentally determined boiling point elevations.

Elevation of boiling point of ether by dissolved $UO_2(NO_3)_2 \cdot 3H_2O$

Vol. ether taken (ml)	wt. UNT added	Concentration (molality)	Mole Ratios $UN:Et_2O:H_2O$	Observed Elevation °C	Calc. elevation for 1 species °C
75	8.000	0.3414	1:41.3:3	0.595	0.661
75	10.000	0.4267	1:33.1:3	0.932	0.827
75	12.500	0.5334	1:26.5:3	1.010	1.030
75	15.000	0.6401	1:22.1:3	1.225	1.240
75	17.500	0.7468	1:18.9:3	1.465	1.445
75	22.004	0.9390	1:15.1:3	2.235	-

Table 3.

Elevation of boiling point of ether equilibrated against aqueous uranyl nitrate solution

Vol. ether taken	Concentration (molality)	Mole.Ratios $UN:ET_2O:H_2O$	Observed Elevation °C	Calc. elevation for 1 species °C
75	0.307	1:45.9:5.4	0.475	0.594
75	0.386	1:36.0:5.3	0.720	0.758
65		1:29.0:5.2	0.940	0.940
75	0.572	1:24.1:5.15	1.065	1.130
75	0.859	1:16.5:4.85	1.645	1.660
75	1.145	1:12.5:4.77	2.710	2.19
75	1.435	1:10.05:4.65	4.525	2.71
75	1.695	1:8.57:4.55	5.9	3.19

Table 4.

In fig. XVI there is good agreement between the experimental curve and the theoretical curve for one solute species, except at high concentrations of uranyl nitrate where ideal conditions no longer hold. This indicates that $UO_2(NO_3)_2.3H_2O$ is present in ether as a single species. It cannot therefore be ionized, and the water is evidently tightly bound. No indication is obtained of any solvation of ether, but this is hardly surprising in the circumstances.

Fig. XVII also shows good agreement between the experimental curve and the theoretical curve for one solute species, except at high uranyl nitrate concentrations. This solution however contains 'free' water as well as $UO_2(NO_3)_2.4H_2O$, and it was shown experimentally that a saturated solution of water in ether boiled 0.365° lower than pure ether. If this 'free' water is affecting the experimental results to this extent it implies that the number of solute species rises from 1.22 at a mole ratio of 16 to 1.46 at a mole ratio of 46. Conductivity experiments prove that this is not due to ionisation, and the coincidence of the experimental curve with that theoretical curve for one solute species which disregards the 'free' water looks more than fortuitous. It appears, therefore, that only one solute species exists in the solution - presumably $UO_2(NO_3)_2.4H_2O$ - and that sufficient attraction exists between it and the 'free' water to prevent this water from affecting the boiling point.

Water-saturated solutions of uranyl nitrate in ether, and solutions of $UO_2(NO_3)_2.3H_2O$ in ether, therefore, are substantially unionised.

Conductivities and Viscosities

The conductivities of water-saturated solutions of uranyl nitrate in several solvents have been measured by Mr. H.A.C. McKay, using conductivity cells of orthodox design and an A.C. bridge, over the concentration range 0.001 m to 1.0 m. The equipment was of much greater precision than was necessary for the purpose. The usual correction for the conductivity of the solvent was applied. The viscosities were measured at 25°C using simple Ostwald viscometers and water and aniline as standard liquids. Density determinations, required for the viscosities and for the interconversion of concentration scales, were made simply by weighing 10 ml. samples from a pipette. The viscosities were measured by Mr. M. Rigg. Any analyses for uranium content were carried out as described in Chapter V.

The results of the conductivity and viscosity measurements are shown in Table V.

Table V - Conductivities and viscosities of water-saturated organic uranyl nitrate solutions

Solvent	UN concentration		Equivalent conductivity (λ)	Viscosity(η) Centipoises
	molality (m_{UN})	molarity (M_{UN})		
Diethyl Ether	0	0	-	0.250
	0.0.08	0.00765	0.0089	-
	0.0216	0.0153	0.0082	-
	0.0430	0.0305	0.0103	-
	0.108	0.765	0.0143	-
	0.0120	0.084	-	0.280
	0.171	0.120	-	0.295
	0.221	0.153	0.0182	-
	0.240	0.168	-	0.314
	0.491	0.336	0.0426	0.457
	0.786	0.525	0.133	-
	1.033	0.672	0.182	-
	1.32	0.840	0.308	1.07
	2.00	1.20	0.315	2.20
	3.08	1.68	0.245	5.46

Solvent	m_{UN}	M_{UN}	λ	η
β ethoxyethyl ether	0	0	-	0.71
	0.00080	0.00068	0.0090	-
	0.0080	0.0068	0.033	-
	* 0.0232	0.020	-	0.73
	* 0.080	0.0675	0.075	-
	* 0.141	0.113	-	0.78
	* 0.935	0.680	0.201	2.4
	* 2.12	1.42	-	9.5
	3.66	2.04	0.134	29
β-β' dibutoxyethyl ether	0	0	-	2.21
	0.282	0.241	0.012	3.4
	0.595	0.482	0.039	5.8
	0.871	0.689	0.061	9.5
	1.072	0.826	0.068	-
	1.313	0.964	0.067	19.0
methyl isobutyl ketone	0	0	-	0.563
	0.00362	0.00290	0.91(?)	-
	0.0090	0.00725	0.971	-
	0.0187	0.0145	0.920	0.594
	0.0370	0.0290	0.867	0.620
	0.092	0.0725	0.899	-
	0.1885	0.145	0.915	0.723
	0.385	0.290	1.16	0.916
	1.03	0.725	0.842	1.91
	1.56	1.04	0.615	3.29
	2.36	1.45	0.400	6.46

* Solns. not quite water-saturated

Solvent	m_{UN}	M_{UN}	λ	η
	0	0	-	3.59
	0.147	0.0996	2.06	-
	0.426	0.284	2.40	-
Isobutyl	1.00	0.625	1.77	-
alcohol	1.18	0.725	1.77	-
	1.70	0.996	1.16	-
	2.62	1.43	0.695	-
	3.03	1.58	0.668	-
	0	0	-	3.24
Isoamyl	0.246	0.183	0.601	4.40
alcohol	0.492	0.357	0.501	5.74
	0.738	0.530	0.377	7.05
	0.984	0.703	0.303	8.62

An estimate of the degree of ionisation of the uranyl nitrate may be obtained from these results using the Walden formula[3]

$$\lambda_\infty \eta_0 = K \qquad (\lambda_\infty = \text{equiv. const. at infinite dilution}$$
$$= \text{viscosity of pure solvent})$$

and combining this with

$$\lambda / \lambda_\infty = \alpha \qquad (\alpha = \text{degree of dissociation})$$

$$\text{Hence} \quad \alpha = \frac{\lambda \eta_0}{K}$$

A more recent formula, which is more generally applicable, is that of Noyes and Falk[4]

$$\alpha = \frac{\lambda}{\lambda_\infty} \left(\eta / \eta_0 \right)^k$$

where λ and η refer to the solution, and k is a const., usually a little less than unity, but equal to unity for ions of low mobility. It has been assumed to be unity for this purpose.

Hence $\alpha = \dfrac{\lambda\eta}{\lambda_\infty\eta_0} = \dfrac{\lambda\eta}{K}$ where K is the const. from the Walden formula.

Computations from data given in Harned and Owen[7] ("The Physical Chemistry of Electrolytic Solutions") leads to a value of K = 60 with a possible error of not more than ± 30%. So values of $\lambda\eta/60$ are taken as being approximately equal to the degree of dissociation of the uranyl nitrate. In fig. XVIII these values are plotted against concentration. Since no viscosity determinations were made for isobutyl alcohol solutions it was assumed that the viscosity curve for uranyl nitrate in this solvent runs parallel to the corresponding curve for isoamyl alcohol solutions. The slight water-deficiency in some of the β ethoxyethyl ether solutions seems, on grounds of experience, unlikely to have much effect. The observed conductivities are low, but are almost certainly due to the uranyl nitrate itself and not to nitric acid formed by hydrolysis, as measurements on organic nitric acid solutions have shown.

Fig. XVIII shows that the degree of ionisation was almost always small, in agreement with the conclusions from the boiling point experiments. In isobutyl alcohol $\lambda\eta/60$ did exceed 10%, but this solvent dissolves a great deal of water. In all other solvents studied $\lambda\eta/60$ never exceeded 10% and was frequently several powers of 10 smaller. It seems safe to conclude that uranyl nitrate is present largely in an unionised form in organic solvents, and that ionisation in the organic phase will not effect equilibria between phases unless the concentration of uranyl nitrate exceeds $m_{UN} = 1.0$ when $\lambda\eta/60$ often lies between 1% and 10%.

The general shapes of the curves of fig. XVIII conform to the usual pattern for conductivities in solvents of low dielectric constant, where, as concentration increases, the conductivity passes first through a minimum at a concn. of approx. $3.5 \times 10^{-5}D^3$

equivs./litre (D = dielectric const.) and then through a maximum at about 1 equiv./litre[5]. It appears from the results presented here that the conductivity maximum is entirely a viscosity effect; there is no corresponding maximum in the ionisation curve.

The steep rise in λ and $\lambda\eta/60$ with concentration is a phenomenon about which little is understood. The theory of Fuoss and Kraus[6], which postulated triple ions, applies to 1:1 electrolytes in dioxane-water mixtures, and correlation with the systems studied here is difficult. It is evident however that, at high concentration, the uranyl nitrate modifies the medium in some way to make it more conducting.

References to Chapter III.

1. Katzin and Sullivan,	AECD 2537
2. Swietoslowski,	Physical Methods of Organic Chemistry, Interscience, New York 1945 (Vol. 1).
3. Walden,	Z.Physik.Chem., 1906, <u>55</u>, 207-249.
4. Noyes and Falk,	J.Amer.Chem.Soc., 1912, <u>34</u>, 454.
5. Walden,	Electrochemie nicht-wasserigen losungen (Barth, Leipzig, 1924)
6. Fuoss and Kraus,	J.Amer.Chem.Soc., 1933, <u>55</u>, 1019.
7. Harned and Owen,	The Physical Chemistry of Electrolytic Solutions, Reinhold, New York, 1943.

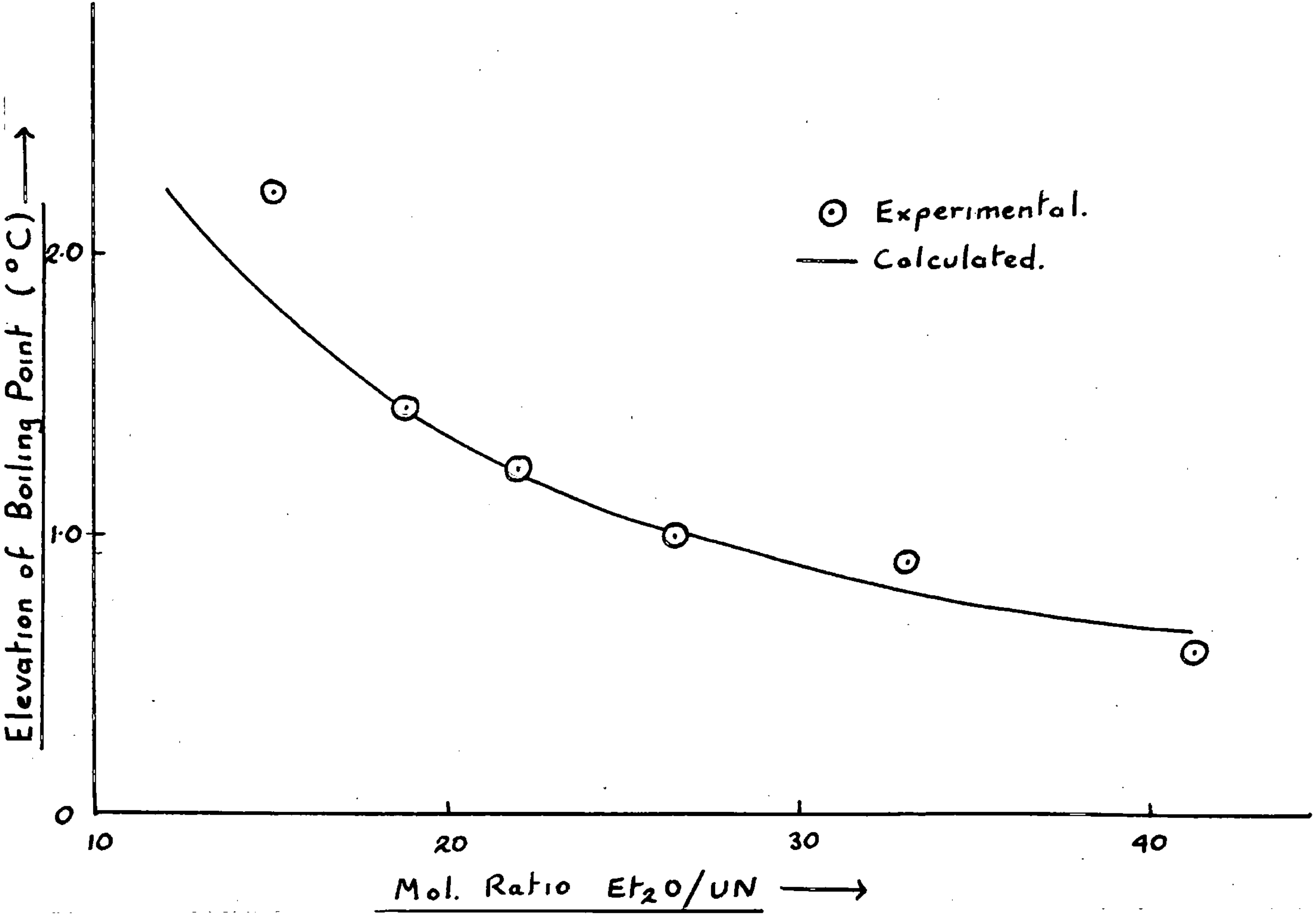


FIG. XVI. SOLUTIONS OF $UO_2(NO_3)_2 \cdot 3H_2O$ IN DIETHYL ETHER.

FIG. XVII. SOLUTIONS OF $UO_2(NO_3)_2 \cdot 4H_2O$ IN WATER-SATURATED ETHER.

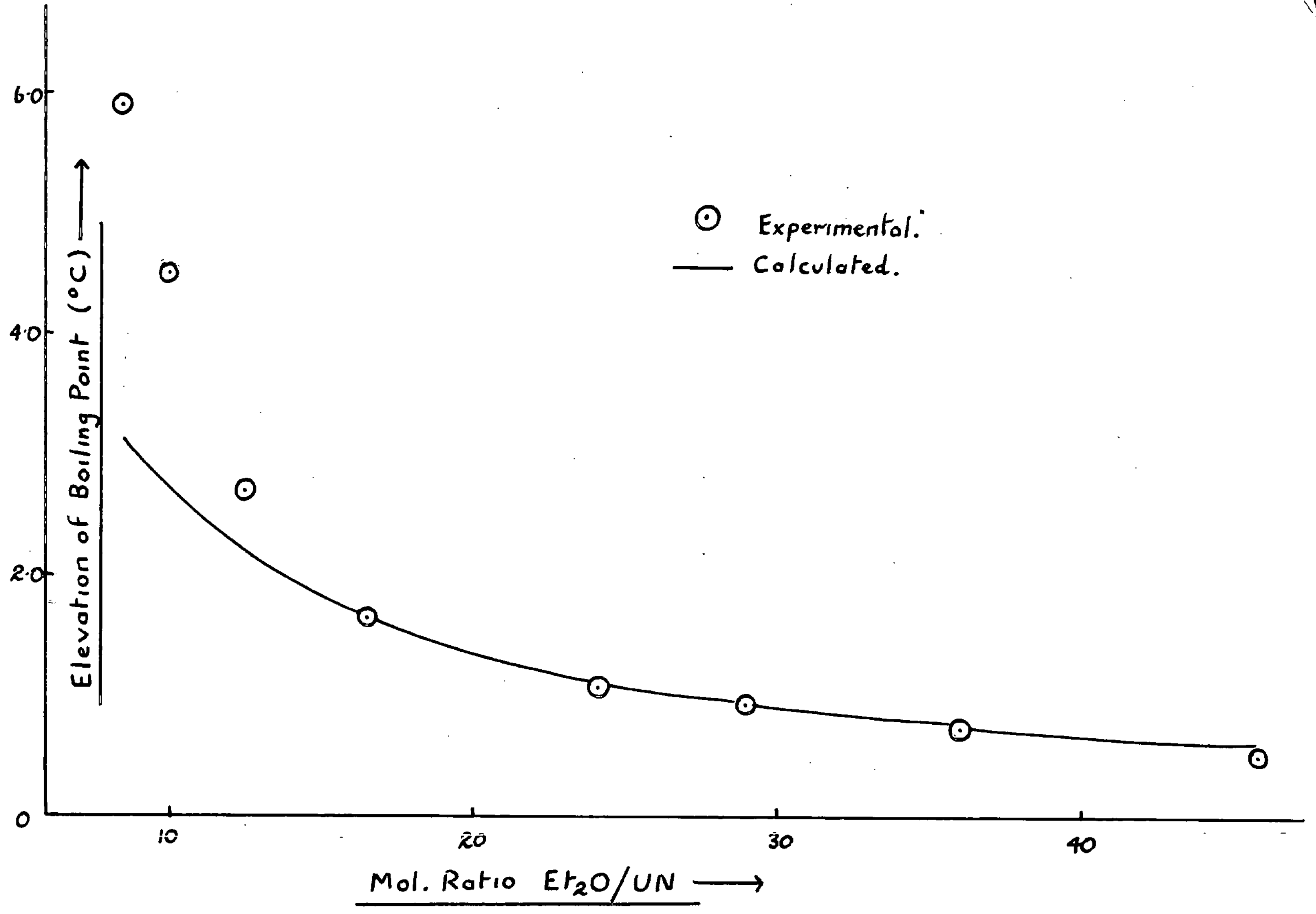
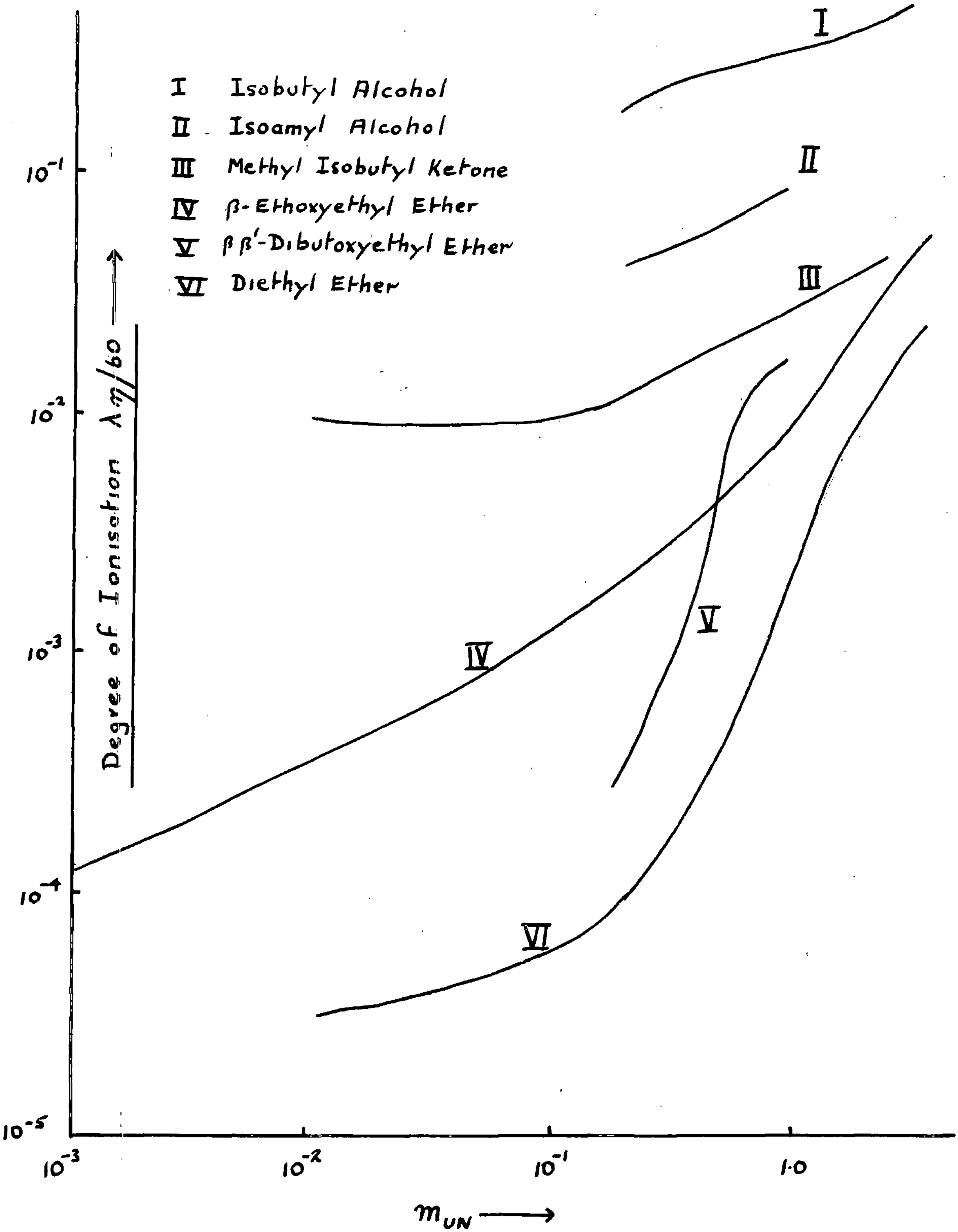


FIG. XVIII. DEGREE OF IONISATION OF URANYL NITRATE IN ORGANIC SOLVENTS.



Chapter IV. Vapour Pressures of aqueous Uranyl Nitrate Solutions

Robinson, Wilson and Ayling[1] have determined the vapour pressure, and hence the osmotic and activity coefficients, of uranyl nitrate in aqueous solution up to 2.035 molal by an isopiestic method. The behaviour of uranyl nitrate is normal for a 2:1 nitrate up to this concentration. Using the apparatus to be described in Chapter VII, this has been extended up to saturation at 3.24 molal. Table 6 shows the results, and figs. XIX and XX are plots of water activity and osmotic coefficient respectively against concentration, with both the earlier and the new values. The experimental technique used was the same as that described in Chapter VII under the heading "testing".

Vapour Pressures of Aqueous Uranyl Nitrate Solutions

Concentration (m)	Vapour pressure mm.	Water Activity (a_w)	Osmotic coefft. (ϕ)	Temp. °C
3.240	17.489	0.7632	1.750	25.0
2.794	18.276	0.7695	1.736	25.0
2.283	19.316	0.8132	1.675	25.0

Table 6.

Figs. XIX and XX show that in concentrated aqueous solution uranyl nitrate ceases to behave like a normal 2:1 nitrate. Its vapour pressure is higher than that which would be obtained by an extrapolation of the earlier values. This result has since been confirmed by Robinson[2], using his isopiestic method. His results are in good agreement with those in Table VI. Fig. XX shows the abnormal behaviour more clearly. $\phi = \left(\frac{-42.606}{m} \log_{10} a_w.\right)$

The vapour pressure of saturated uranyl nitrate corresponds to an activity coefft. of 2.25. If the salt behaved normally right up to saturation, the activity coefft. of the saturated solution would be about 2.64. This discrepancy can only be explained by association in the solution to an appreciable extent, giving ion-pairs on undissociated molecules

$$UO_2^{++} + 2NO_3^- \rightleftharpoons UO_2NO_3^+ + NO_3^- \rightleftharpoons UO_2(NO_3)_2$$

$$\text{or} \quad UO_2^{++} + 2NO_3^- \rightleftharpoons UO_2^{++}.2NO_3^-$$

To explain the magnitude of the effect would require so large a proportion of the $UO_2NO_3^+$ species, if it alone were responsible, that some association into neutral $UO_2(NO_3)_2$ molecules seems probable. If all the association proceeded to $UO_2(NO_3)_2$, the saturated solution would then contain 16% of neutral $UO_2(NO_3)_2$ molecules. Unfortunately no data exist which enable any calculations of the proportions of $UO_2NO_3^+$ and $UO_2(NO_3)_2$ to be made, but the experiments indicate the probable existence, in concentrated aqueous solution, of neutral $UO_2(NO_3)_2$ molecules. This fact is of considerable interest when organic uranyl nitrate solutions are considered. If neutral molecules can exist in aqueous solution, then their passage into organic solution is not surprising.

A table of activity coefficients of uranyl nitrate in aqueous solution is given in refs. 1 and 2.

References to Chapter IV

1. Robinson, Wilson and Ayling,	J.Amer.Chem.Soc., 1947, 64, 1469-1471.
2. Robinson and Lim,	J.Chem.Soc., to be published.

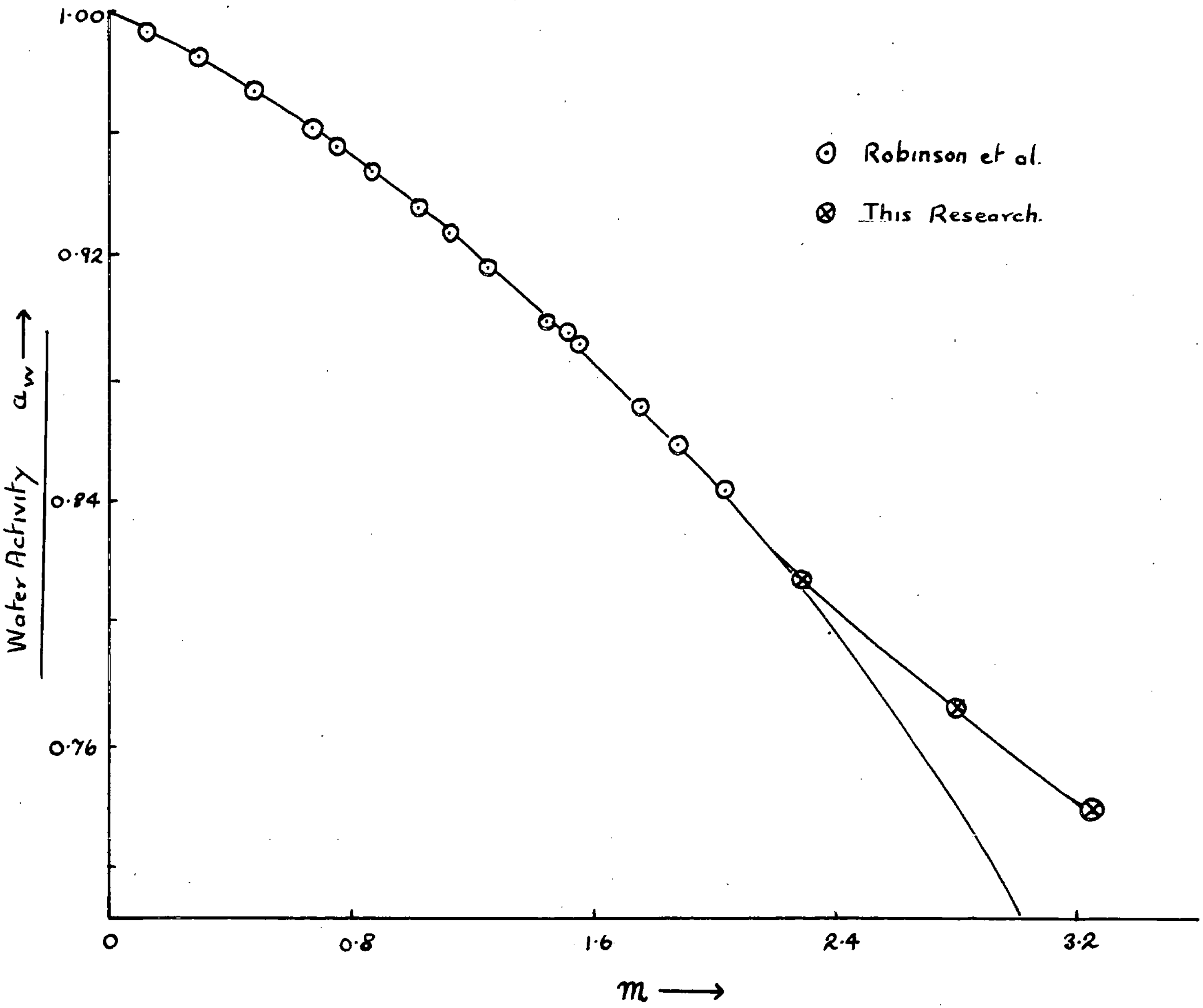
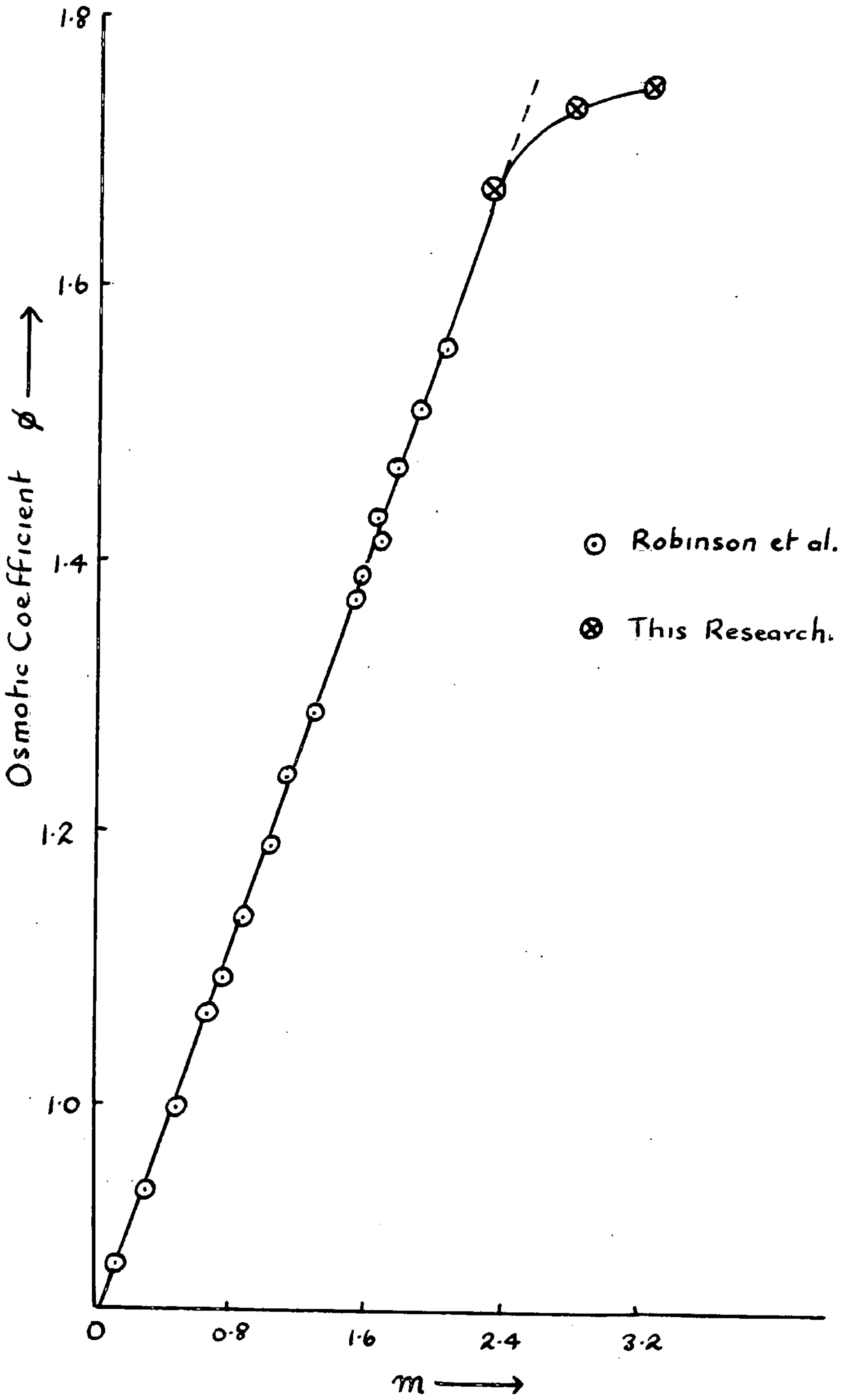


FIG. XIX. WATER ACTIVITY OF AQUEOUS URANYL NITRATE SOLUTIONS.

FIG. XX. OSMOTIC COEFFICIENTS OF AQUEOUS URANYL NITRATE SOLUTIONS.



Chapter V. The Partition of Uranyl Nitrate between water and organic solvents

It has been shown in Chapter III that uranyl nitrate occurs principally as an unionised hydrate in the organic phase of a partition equilibrium. The degree of hydration is constant for ethers, ketones and esters, and frequently equal to 4. That a mixture of different hydrates may be present in the organic phase is more than probable. Indeed in those cases where the degree of hydration is non-integral this is virtually certain. Nevertheless the phase may be treated stoichiometrically as containing a single hydrate whose composition is known, for the purposes of thermodynamics.

Although the organic phases of partition equilibria contain appreciable concentrations of water, the aqueous phases in general contain so little organic solvent that this may be neglected. The aqueous phase may thus be treated simply as a pure water solution of uranyl nitrate. It has already been established (Chapter IV) that dissociation is incomplete at the highest concentrations. A detailed description of the equilibria set up in the partition equilibrium may thus be given.

Aqueous phase

$$UO_2^{++} + 2NO_3^- \rightleftharpoons UO_2(NO_3)_2$$

Organic phase

$$UO_2(NO_3)_2 \cdot xH_2O \rightleftharpoons UO_2^{++} + 2NO_3^- + xH_2O$$

These equilibria are, however, completely catered for by the activity coefficients for the respective phases, provided that the stoichiometric compositions of the two phases are adhered to. It is thus justifiable to simplify the treatment of the system, and assume that an equilibrium

$$UO_2^{++} + 2NO_3^- + xH_2O \rightleftharpoons UO_2(NO_3)_2 \cdot xH_2O$$

is set up between the components of the two phases. This leads to an equilibrium constant

$$\frac{[UO_2^{++}][NO_3^-]^2[H_2O]^x}{[UO_2(NO_3)_2 \cdot xH_2O]} = \text{constant} \qquad (1)$$

the quantities in square brackets denoting the appropriate activities. If γ represents the mean molal activity coefficient of uranyl nitrate in the aqueous phase, and m its molality, then

$$[UO_2^{++}][NO_3^-]^2 = 4\,m^3\gamma^3 \qquad (2)$$

If γ_{UN} and m_{UN} are the activity coefficient and molality respectively, of uranyl nitrate in the organic phase, then

$$[UO_2(NO_3)_2 \cdot xH_2O] = m_{UN}\gamma_{UN} \qquad (3)$$

Hence, if a_w is the water activity in the aqueous phase,

$$\frac{4\,m^3\gamma^3\,a_w^{\,x}}{m_{UN}\gamma_{UN}} = \text{constant} \qquad (4)$$

$$\text{i.e.} \qquad m^3\gamma^3\,a_w^{\,x} = K\,m_{UN}\gamma_{UN} \qquad (5)$$

$$\text{or} \qquad 3\ln m\gamma a_w^{\,x} = \ln K + \ln m_{UN}\gamma_{UN} \qquad (6)$$

A small correction to the equations is necessary when they are applied to the experimental results. The quantity m_{UN} applies to the water-saturated organic phase and so should be expressed as gram-molecules per 1000 grams of water-saturated solvent. The uranyl nitrate concentration in the organic phase will nevertheless be expressed as gram-molecules per 1000 grams of dry solvent to keep it in line with the results of Chapters II and III, and this will have the effect of introducing a constant factor differing only slightly from unity, which can be absorbed in the constant K. The same argument applies to the quantity m.

To use equation (6) values of γ and a_w will be taken for a pure aqueous uranyl nitrate solution, ignoring the small quantity of dissolved organic solvent. At sufficient dilutions γ_{UN} may be taken as approximately equal to unity. Hence a plot of $\ln m\gamma a_w^{x/3}$ against $\ln m_{UN}$ should give a straight line of slope $1/3$, and deviations from this straight line at higher concentrations will allow γ_{UN} to be evaluated. The assumption that $\gamma_{UN} = 1$ for dilute solutions is abundantly justified by experiment, the slope of the $\ln m\gamma a_w^{x/3} / \ln m_{UN}$ curves being accurately $1/3$ for all solvents in dilute solution.

It is on this theoretical basis that the experimental data on the partition equilibria will be treated.

Experimental methods

20 mls. of an aqueous uranyl nitrate solution were shaken with 20 mls. of organic solvent in a thermostat held at $25 \pm 0.01^\circ C$ for at least 30 minutes. The two layers were then separated and centrifuged. For very high uranyl nitrate concentrations it was sometimes necessary to add solid uranyl nitrate hexahydrate crystals to the solutions.

For analysis 2 ml. samples of each layer were taken, except in the case of very dilute solutions where larger volumes were necessary. The samples from aqueous phases were evaporated in silica crucibles under infra-red lamps and converted to U_3O_8 in a furnace at 800°C, the furnace having ready access of air. Samples from organic phases, and from aqueous phases too in the case of partitions involving cyclohexanone, were evaporated with excess water in beakers on a hotplate before being transferred to silica crucibles and baked to U_3O_8 at 800°C. This procedure was necessary to prevent minor explosions. Very dilute organic phase samples ($<$ 0.03 m.) were analysed using a 'Spekker' absorptiometer. Solvent was removed by oxidation with HNO_3 and $HClO_4$, the residue dissolved in HNO_3, precipitated with NaOH and just redissolved in HNO_3. The colour of the solution was then enhanced by addition of H_2O_2. These spectroscopic analyses were performed by Miss V. Mitchell. Each analysis was done in duplicate.

Figs. XXI and XXII show the results plotted as log m_{UN} against log m for the nine solvents investigated. The results are shown in tabular form in appendix II, where the worker who obtained the individual results is also indicated.

Fig. XXIII shows the plot of log $m \gamma a_w^{x/3}$ against log m_{UN}. In dilute solutions the slope is $1/3$ for each solvent, thus justifying the $\gamma_{UN} = 1$ assumption. For most solvents the highest point measured corresponds to saturation with respect to uranyl nitrate. In the case of $\beta\beta'$ dibutoxyethyl ether, however, a solid solvated hydrate separates out before this point is reached. In the case of diisopropyl ether, the most concentrated organic solutions are supersaturated with respect to a compound which analyses to $UO_2(NO_3)_2 \cdot 2.5\ Pr_2O \cdot 4\ H_2O$, and this crystallises out on standing.

The accuracy of the results is approximately ± 2% with larger deviations at low concentrations. Comparison is possible in a number of instances with other work. For diethyl ether the results are in good agreement with the accurate work of Lofthouse and Smith[1] at 18°C, and in fair agreement with the results of Guempel[2], Misciatelli[3], and Katzin and Sullivan[4]. For methyl isobutyl ketone there is good agreement with the results of Katzin and Sullivan.

A small disturbing effect is the hydrolysis of uranyl nitrate in aqueous solutions, which at 0.1 m. occurs at the extent of

3-4%, as shown by a pH of 2.46. This is the lowest concentration used, and hydrolysis should be smaller in more concentrated solutions. The neglecting of this small effect is justified by the agreement between experiment and theory shown in Fig. XXIII. The values of $m\gamma a_w^{x/3}$ used are based on the measurements of Robinson and Lim[5] and of Robinson, Wilson and Ayling[6].

In the case of diethyl ether the solubility of the ether in the aqueous phase is really too large to be neglected (6%). In calculating $m\gamma a_w^{x/3}$ this leads to two different sets of figures if the phase is treated as 100% aqueous or only 94% - e.g. at $m = 1.61$, $m\gamma a_w^{x/3} = 1.40$ or 1.21. The former course has been adopted but the choice is arbitrary.

Activity coefficients and solvation in the organic phase

The departure from linearity of Fig. XXIII at high concentrations enables values of γ_{UN} to be read directly off the curves. The linear parts of the curves are extrapolated and then γ_{UN} is equal to the ratio of m_{UN} extrapolated to m_{UN} experimental for a given value of $m\gamma a_w^{x/3}$. Figs. XXIV and XXV show these results plotted, and show that γ_{UN} rises to very high values as the uranyl nitrate concentration (m_{UN}) increases. They follow, very approximately, a law

$$\log \gamma_{UN} = K\, m_{UN} \qquad (7)$$

where K depends on the solvent. An empirical relation of this type is often found for solutions of unionised substances.

Since ionisation in the organic phase is small, the greater part of the increase in γ_{UN} with m_{UN} must be due to attraction between solvent and solute molecules. Such solvation might be expected on general chemical grounds, and may take place either by direct coordination of the solvent to the uranium atom, or by hydrogen bonding between the solvent - always oxygenated - and the water of hydration, or both.

An estimate, approximate only, of the extent of such solvation can be obtained. Neglecting the small degree of ionisation in the organic phase, and the association in the aqueous phase, an equilibrium may be postulated:-

$$UO_2(NO_3)_2.xH_2O.nS \rightleftharpoons UO_2^{++} + 2NO_3^- + xH_2O + nS$$

This gives an equilibrium constant:-

$$\frac{[UO_2^{++}]\,[NO_3^-]^2\,[H_2O]^x\,[S]^n}{[UO_2(NO_3)_2.xH_2O.nS]} = \text{constant}$$

Substituting the true mole fractions of $[S]$ and $[UO_2(NO_3)_2.xH_2O.nS]$ in the organic phase, i.e.

$$\frac{m_s - nm_{UN}}{m_s - (n-1)m_{UN} + m_{fw}} \qquad \text{and} \qquad \frac{m_{UN}}{m_s - (n-1)m_{UN} + m_{fw}}$$

where $m_s = 1000/Ms$

Ms = molecular wt. of solvent

m_{fw} = molality of free water - water uncombined with uranyl nitrate.

Putting also that $[UO_2{++}]\,[NO_3^-]^2\,[H_2O]^x = 4m^3\,\gamma^3\,a_w^{\,x}$, we have that

$$m^3\,\gamma^3\,a_w^{\,x} = \frac{\text{const.}\ m_{UN}[m_s - (n-1)m_{UN} + m_{fw}]^{n-1}}{(m_s - nm_{UN})^n} \qquad (8)$$

when $m_{UN} = 0$, $\gamma_{UN} = 1$. Hence the const. has the value

$$\frac{Km_s^{\,n}}{(m_s + m_{fw})^{n-1}} \quad \text{where K has its previous significance.}$$

$$\text{Hence} \quad \gamma_{UN} = \frac{[1 - (n-1)m_{UN}/(m_s + m_{fw})]^{n-1}}{(1 - nm_{UN}/m_s)^n} \qquad (9)$$

which reduces to (7) when m_{UN} is small.

Values of n calculated from (9) will have the significance of stoichiometric solvation numbers, since in reality a whole series of solvated hydrates may be formed . They are of interest therefore principally as a measure of the extent to which different solvents are attracted to the hydrated uranyl nitrate molecules. In calculating values of n from (9) a doubt arises about the value of m_{fw}. It may be equal to the solubility of water in the pure solvents (m_w^o), or it may be equal to zero if the assumption is made that all the water present is bound to the uranyl nitrate or the solvent. Table 7 shows values of n for the different solvents used, and similar figures are obtained using either assumption regarding m_{fw}, except in the case of cyclohexanone. They tend to decrease with increasing values of m_{UN}, and in the order ketones > ester > ethers.

Table 7 - Solvation of uranyl nitrate in the organic phase

Solvent	m_s	m_{fw}	m_{UN}							
			0.2	0.5	0.7	1.0	1.5	2.0	2.5	3.0
Diethyl ether	13.5	0.65 0.0					2.4 2.5	3.1 3.2	3.3 3.4	3.2 3.3
Diisopropyl ether	9.76	0.26 0.0			2.7 2.7					
β-butoxyethyl butyl ether	5.73	0.33 0.0	3.5 3.6	4.0 4.1	3.5 3.7	3.1 3.2				
ββ' dibutoxyethyl ether	4.56	0.76 0.0		1.6 1.7	2.2 2.3	2.2 2.3				
ββ' dibutoxyethoxyethyl ether	3.26	2.25 0.0	2.0 2.2	2.4 2.6	2.3 2.5	2.1 2.2	1.8 1.8	1.5 1.5	1.3 1.3	1.0 1.1
Isoamyl acetate	7.67	0.45 0.0		4.3 4.6	4.1 4.3	3.7 3.8				
Diethyl isobutyl ketone	10.0	1.2 0.0	5.1 6.0	5.2 5.9	5.4 6.1	4.9 5.3	4.1 4.3	3.6 3.7		
Cyclohexanone	10.2	3.6 0.0	7.2 11.3	6.9 9.6	6.4 8.4	5.5 6.7	4.6 5.2	3.9 4.2	3.4 3.6	3.0 3.1

No calculations have been made on alcohols in view of the non-linearity of their m_{UN}/m_{H_2O} curves (Chapter III).

The Equilibrium Constant of the Partition

The theoretically deduced law expressing the behaviour of the partition (equation (5)) is true experimentally up to values of $m_{UN} = 0.1$, extending over several powers of 10 (Fig. XXIII). In the case of diethyl ether equation (5) holds up to $m_{UN} = 1.0$. This is probably an anomaly caused by the solubility of diethyl ether in water. Straight lines on the $\log m\gamma a_w^{x/3} / \log m_{UN}$ plots can be obtained even with the a_w term omitted. It is therefore impossible to evaluate the degree of hydration (x) from the partition experiments. It must be obtained by the methods of Chapter III.

Values of K (equation (5)) may be calculated from the linear portions of the plots of Fig. XXIII. From the equation

$$\Delta G^{\circ} = -RT \ln K,$$

ΔG° may be evaluated, but since this quantity contains an arbitrary constant depending on the concentration units,

$$\Delta G^{\circ}_{T} = RT \ln K/K_{o}$$

has therefore been evaluated, where K_o = the constant for dibutyl ether, chosen as a reference substance. Under these circumstances ΔG°_{T} represents the free energy of transfer of hydrated uranyl nitrate from dibutyl ether to the particular solvent concerned. The calculations have been confined to those solvents which show a constant degree of hydration equal to 4.

Values of K and ΔG°_{T} are shown in Table 8.

Table 8 - Equilibrium Constants and Free Energies

Solvent	K	ΔG^{o}_{T} (cals.)
Diethyl ether	2.16	3400
Di-isopropyl ether	84	1000
Dibutyl ether	393	0
β-butoxyethyl butyl ether	11.0	2300
$\beta\beta'$ dibutoxyethyl ethyl ether	0.655	4300
$\beta\beta'$ dibutoxyethoxy ethyl ether	0.0483	5900
Isoamyl acetate	16.8	2100
Methyl isobutyl	1.33	3700
Cyclohexanone	0.0337	6200

A remarkable feature of the values of ΔG^{o}_{T} can be seen if they are plotted against the ratio of the number of atoms of oxygen to the number of atoms of carbon in the solvent concerned, for the series of the ethers, An almost linear relation is obtained, even the poly-ethers falling on the same curve as the mono-ethers. This suggests that the oxygen atoms in a poly-ether act independently of one another in their behaviour towards uranyl nitrate. Fig. XXVI shows this curve.

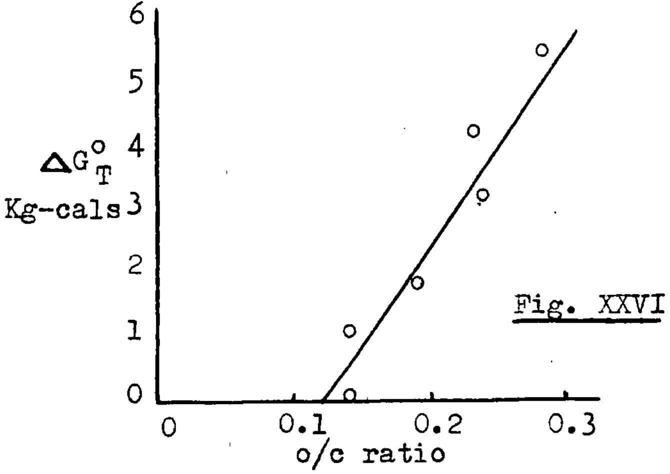


Fig. XXVI

Similar behaviour is seen if the solubility of uranyl nitrate in the organic solvents be plotted against the oxygen-carbon ratios.

Solubility of Uranyl Nitrate Hexahydrate in Organic Solvents

Much information can be obtained from the solubilities of uranyl nitrate hexahydrate in organic solvents measured by Yaffe[7]. A few more solubilities were measured to complete the picture, and to check some of the more doubtful of Yaffe's determinations. Solutions in butyl and hexyl ethers were noticed to decompose, forming a pale yellow precipitate of uranyl peroxide[4]. Experiments showed that dissolved air or ether peroxides caused this decomposition. Yaffé's results for these ethers were checked and found to be too high, presumably due to this decomposition. The new solubilities are shown in Table 9.

Solubiluty of UNH in some organic solvents at 25°C

Solvent	Solubility of UNH (g.UNH/ml) 25°C	Yaffe's value (g.UNH/ml) 20°C
* Dihexyl ether	0.015	0.09
* Dibutyl ether	0.11	0.16
Di-isopropyl ether	0.29	0.09
Methyl alcohol	1.53	-
Ethyl alcohol	1.31	-
n-Propyl alcohol	1.10	-
* sec-octyl alcohol	0.39	-
Ethylene glycol	1.73	-
Glycerol	1.77	-
Diacetone alcohol	0.87	-
n-Propyl acetate	0.75	-
Acetone	1.43	-
Methyl ethyl ketone	1.13	-
* Cyclohexanone	1.08	1.05
* $\beta\beta'$ dibutoxyethoxy ethyl ether	0.87	0.90
Benzaldehyde	0.59	-

Table 9.

The values with an asterisk in table 9 were determined by equilibration and analysis. The remainder were determined simply by adding just sufficient solvent to a known weight of uranyl nitrate.

If plots are made of solubility against number of carbon atoms per molecule for each series of solvents, smooth curves are produced. This was noted by Yaffé[7]. Those solvents which contain more than one oxygen atom per molecule do not fall on the curves, but if plots are made of solubility against the ratio of number of carbon to oxygen atoms in the solvent molecule, then such solvents do fall on the curves. Figs. XXVII - XXIX show such plots for the several types of solvent. This indicates that the oxygen atoms play a definite quantitative role in the dissolution of the uranyl nitrate. Fig. XXX shows, side by side, plots of uranyl nitrate solubility and of water solubility against oxygen/carbon ratio in ethers. The water solubilities behave in the same way as the uranyl nitrate solubilities, indicating that the mode of solution is probably the same in each case.

Detailed examination of the solubilities yields several further facts

(i) Cl, Br, double bonds, and electron-attracting groups in general greatly reduce solubility of UNH

e.g. dichlorodi-isopropyl ether 0.05 g UNH/ml., but
di-isopropyl ether 0.29
vinyl acetate 0.31 but ethyl acetate 0.82.

(ii) Straight-chain compounds show greater solubility than branched chain compounds

e.g. isobutyl propionate 0.31, n-butyl propionate 0.55
isoamyl propionate 0.27, n-amyl propionate 0.37
isobutyl acetate 0.50, sec-butyl acetate 0.61,
n-butyl acetate 0.68

isopropyl acetate 0.64, n-propyl acetate 0.75
2-ethyl butyl alcohol 0.49, methyl amyl alcohol 0.55.

Evidently the further the branching is from the oxygen atom, the smaller is the reduction in solubility.

(iii) Methyl ketones show greater solubility than do symmetrical ketones, there being separate curves for each, converging on acetone (fig. XXIX).

(iv) Alcohols show the greatest solubility.

(v) Esters appear to use only one of their oxygen atoms. The proximity of the oxygen atoms probably explains this.

(vi) Esters of di-acids such as oxalic, succinic, adipic and sebacic acids have low solubilities, the effect being the more marked the nearer the two -COOH groups are together

e.g. n-butyl oxalate 0.09, n-propyl acetate 0.75
amyl succinate 0.25, n-amyl acetate 0.55
butyl adipate 0.40, n-amyl acetate 0.55
ethyl sebacate 0.48, n-amyl acetate 0.55

(vii) Formates, dioxane, $\beta\beta$'dibutoxydiethyl ether, and isopropyl ether as measured by Yaffe have low solubilities. This is due to the formation of a complex with a lower solubility than uranyl nitrate hexahydrate. The new value for isopropyl ether was obtained without formation of the complex.

(viii) Methyl alcohol, glycol, glycerol and acetone show greater solubilities than water.

(ix) Cyclohexanone shows a high solubility, but dimethyl dioxane falls on its curve. Hexoxyethyl ethyl ether also has a high solubility.

(x) The oxygen/uranyl nitrate mole ratio never descends below 2 and is less than 4 only in solvents having high miscibilities with water.

e.g. acetone 2.5 glycerol 2.6 methyl ethyl ketone 3.1 cyclohexanone 3.2.

(xi) The solvent "methyl ethyl ketone + 15% xylene" fits perfectly on to its curve.

References to Chapter V.

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2. Guempel, Bull.Soc.Chim.Belg. 1929, 38, 443.
3. Misciatelli, Gazz.Chim.Ital., 1930, 60, 833.
4. Katzin and Sullivan, AECD 2537 (1948)
5. Robinson and Lim, J.Chem.Soc., to be published.
6. Robinson, Wilson and Ayling, J.Amer.Chem.Soc., 1947, 64, 1469-1471.
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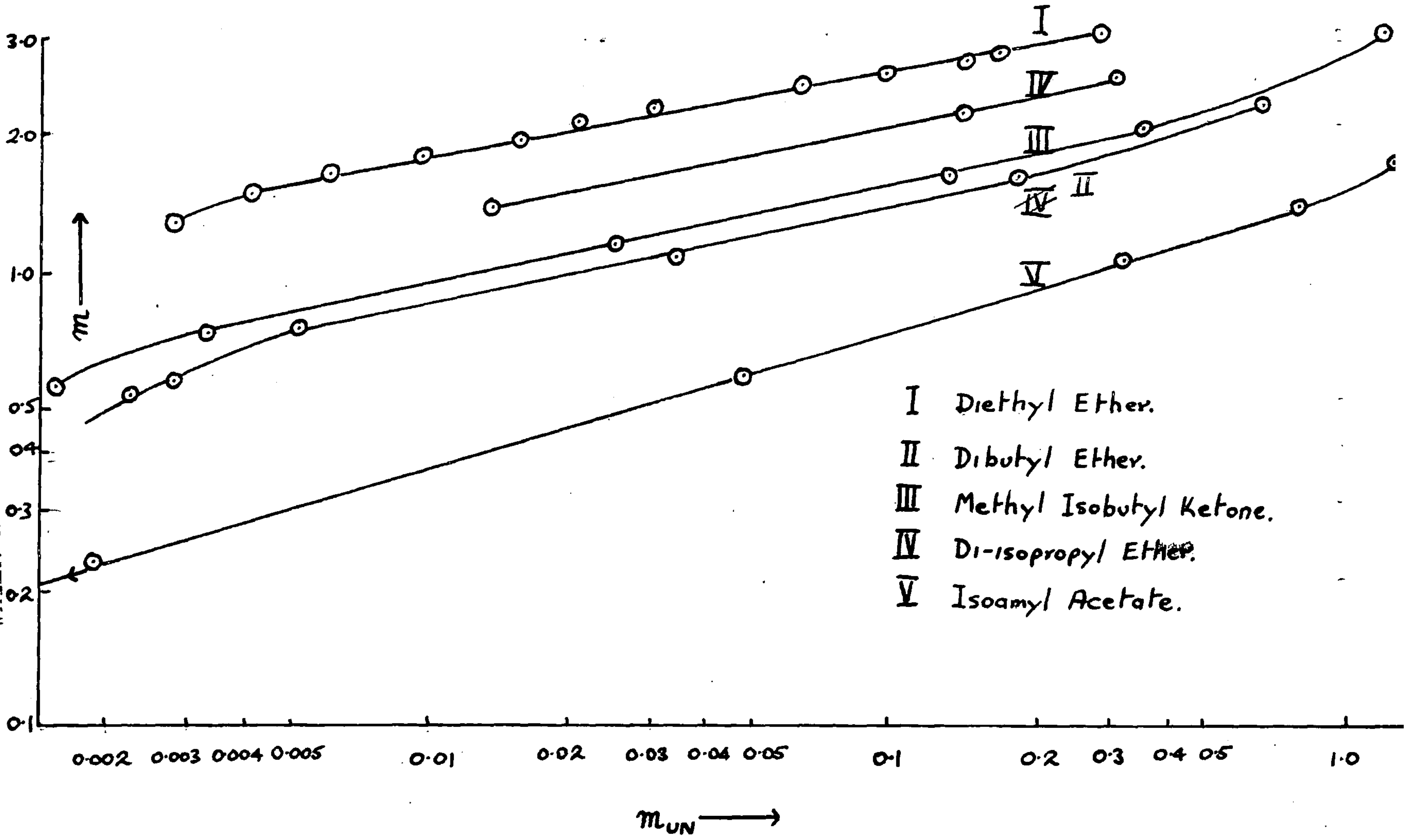


FIG. XXI. PARTITION OF URANYL NITRATE BETWEEN WATER AND ORGANIC SOLVENTS.

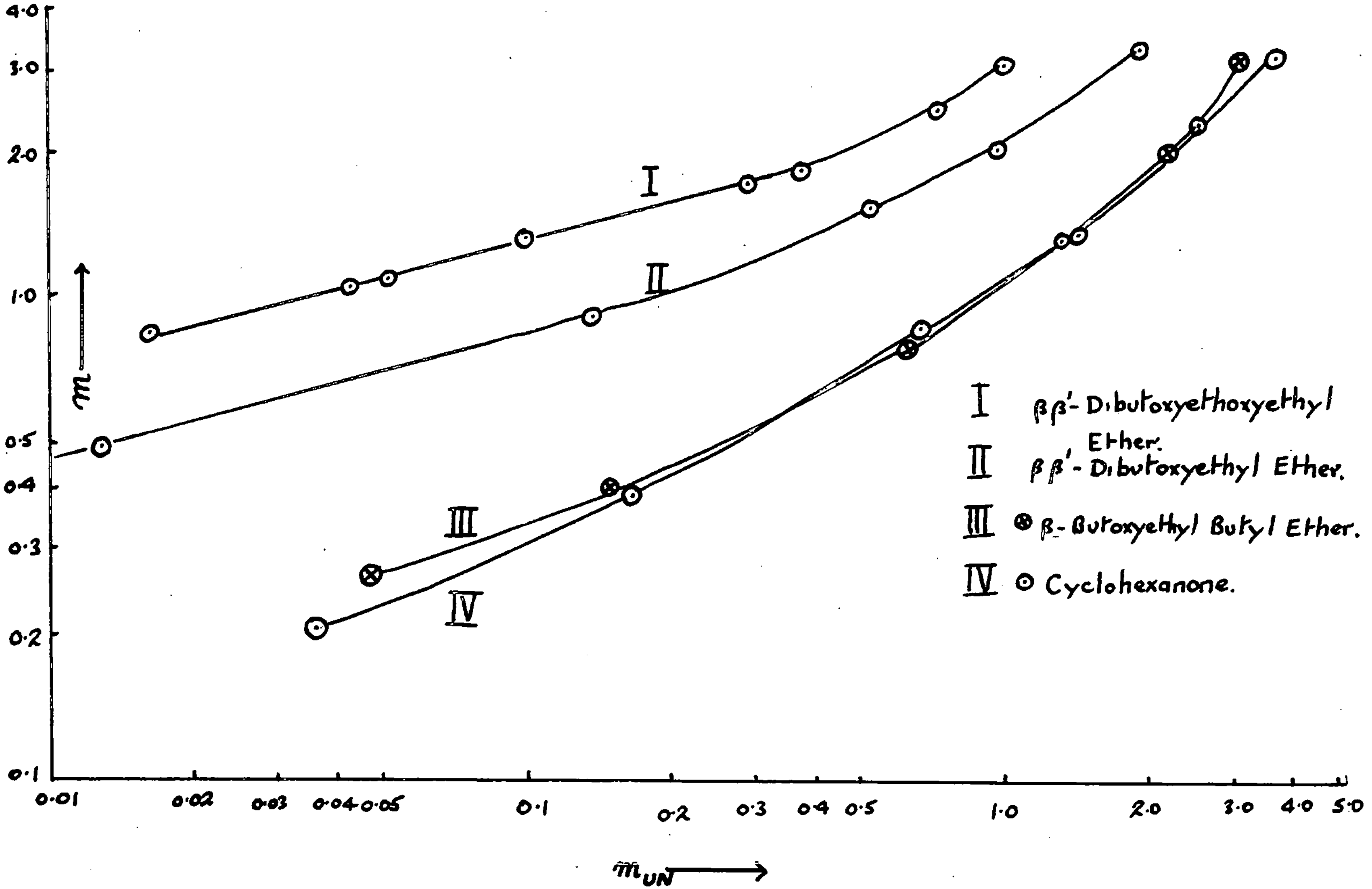


FIG. XXII. PARTITION OF URANYL NITRATE BETWEEN WATER AND ORGANIC SOLVENTS.

FIG. XXIII.

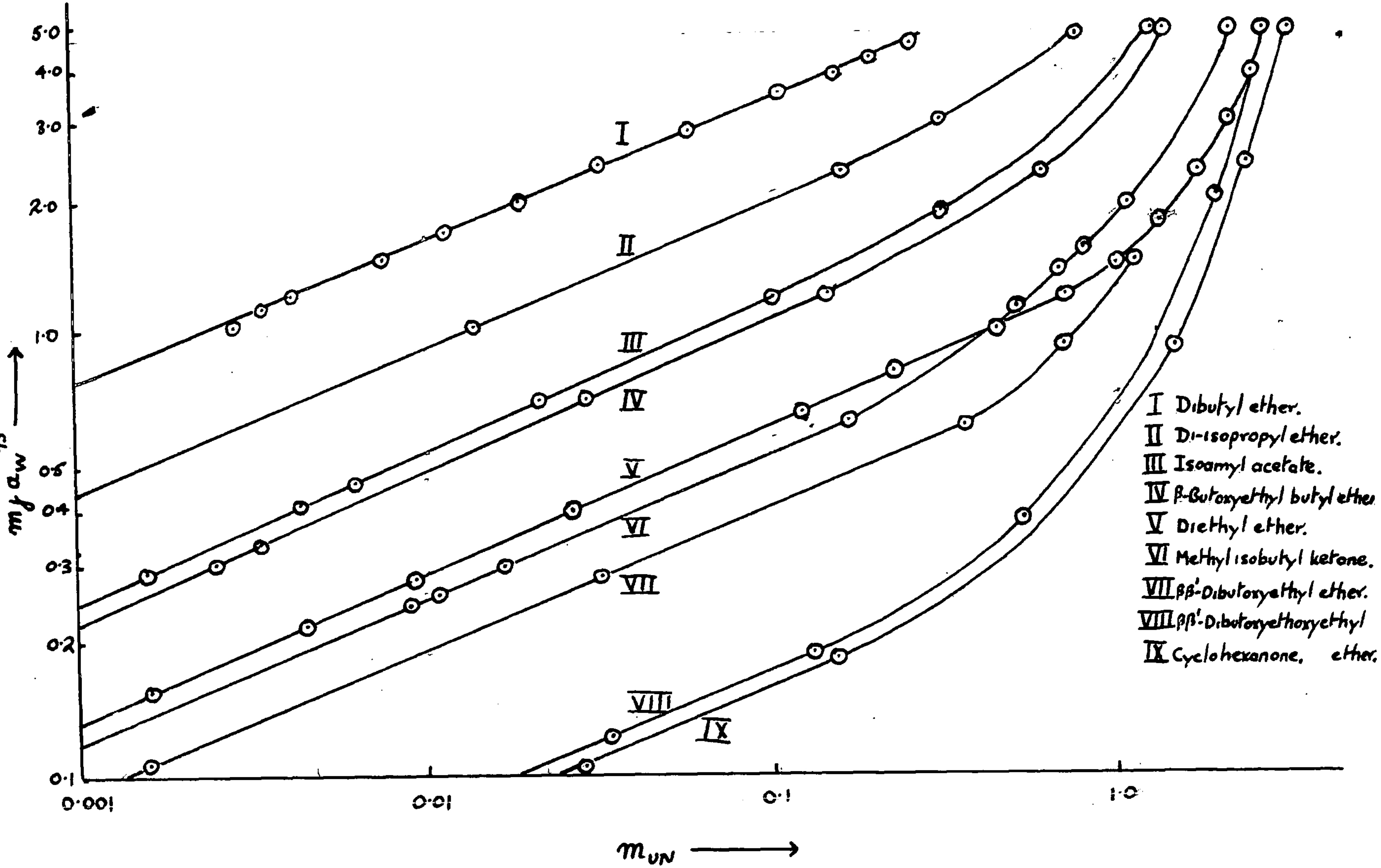

5·0
4·0
3·0
2·0
1·0
0·5
0·4
0·3
0·2
0·1
$m_f a_w^{x/3}$ →
0·001
0·01
0·1
1·0
m_{UN} →
I
II
III
IV
V
VI
VII
VIII
IX
I Dibutyl ether.
II Di-isopropyl ether.
III Isoamyl acetate.
IV β-Butoxyethyl butyl ether
V Diethyl ether.
VI Methyl isobutyl ketone.
VII ββ'-Dibutoxyethyl ether.
VIII ββ'-Dibutoxyethoxyethyl ether.
IX Cyclohexanone.

FIG. XXIV. ACTIVITY COEFFICIENTS OF URANYL NITRATE IN ORGANIC PHASES.

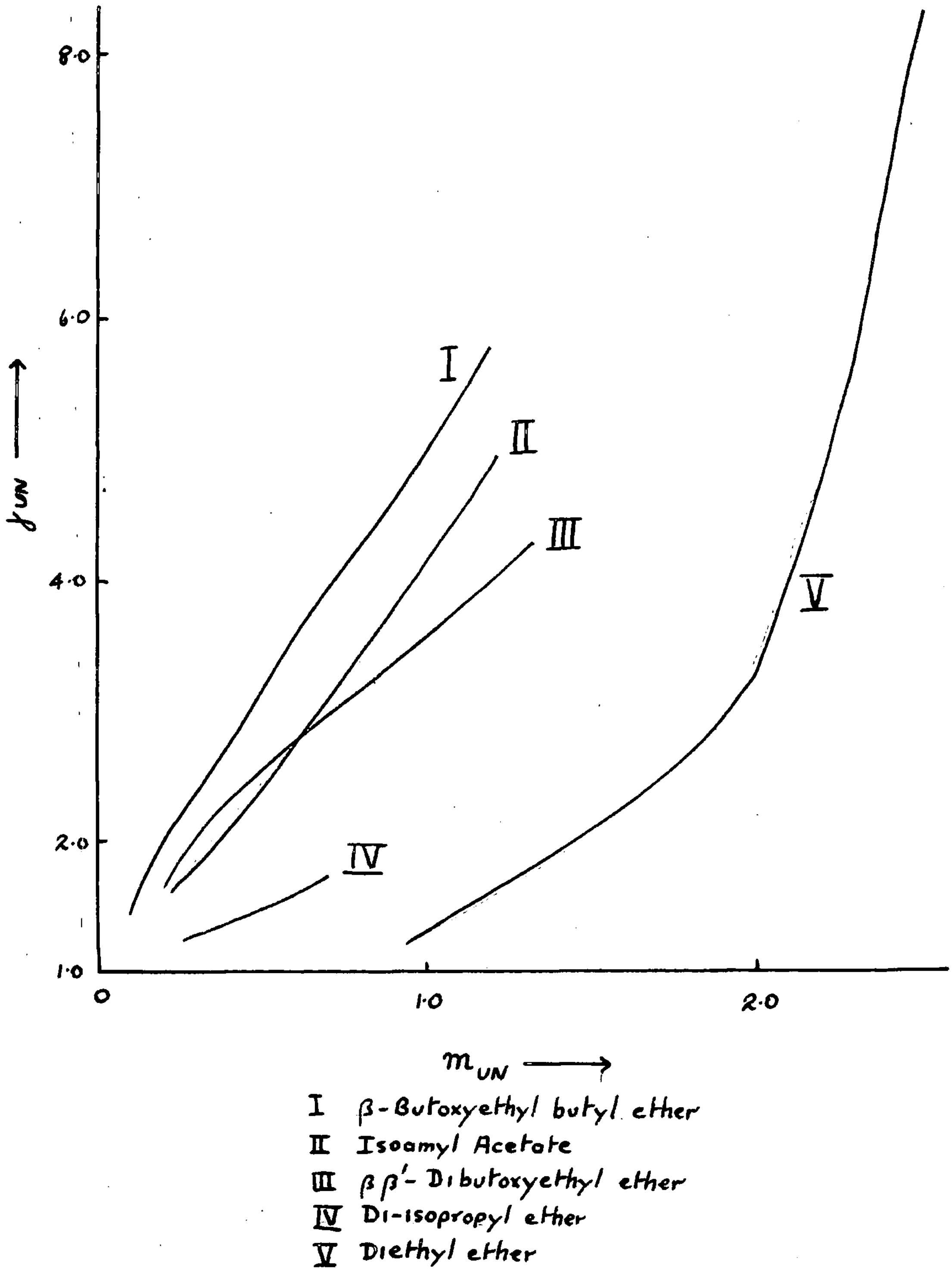


FIG. XXV. ACTIVITY COEFFICIENTS OF URANYL NITRATE IN ORGANIC PHASES.

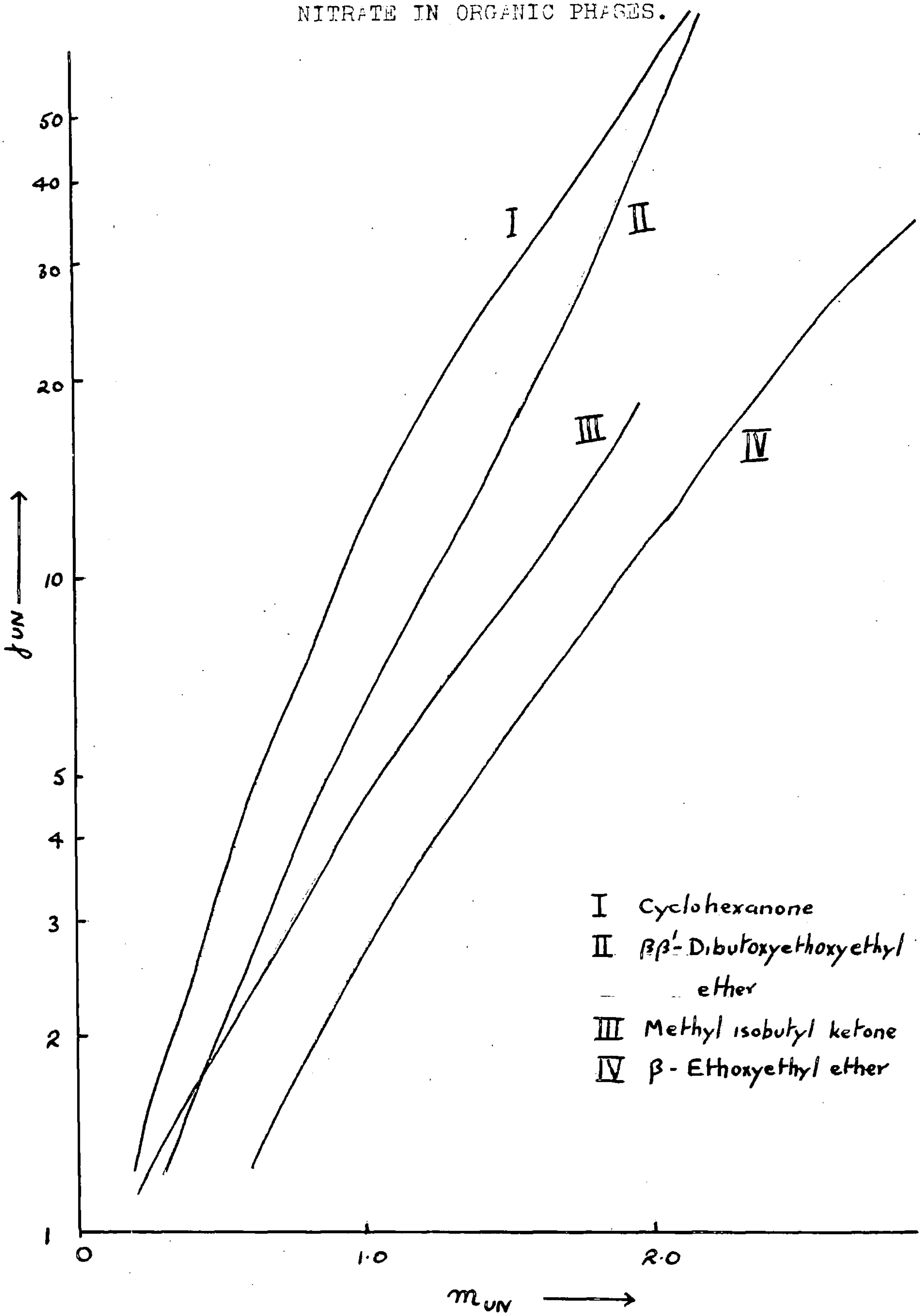


FIG. XXVII. SOLUBILITY OF URANYL NITRATE IN ETHERS.

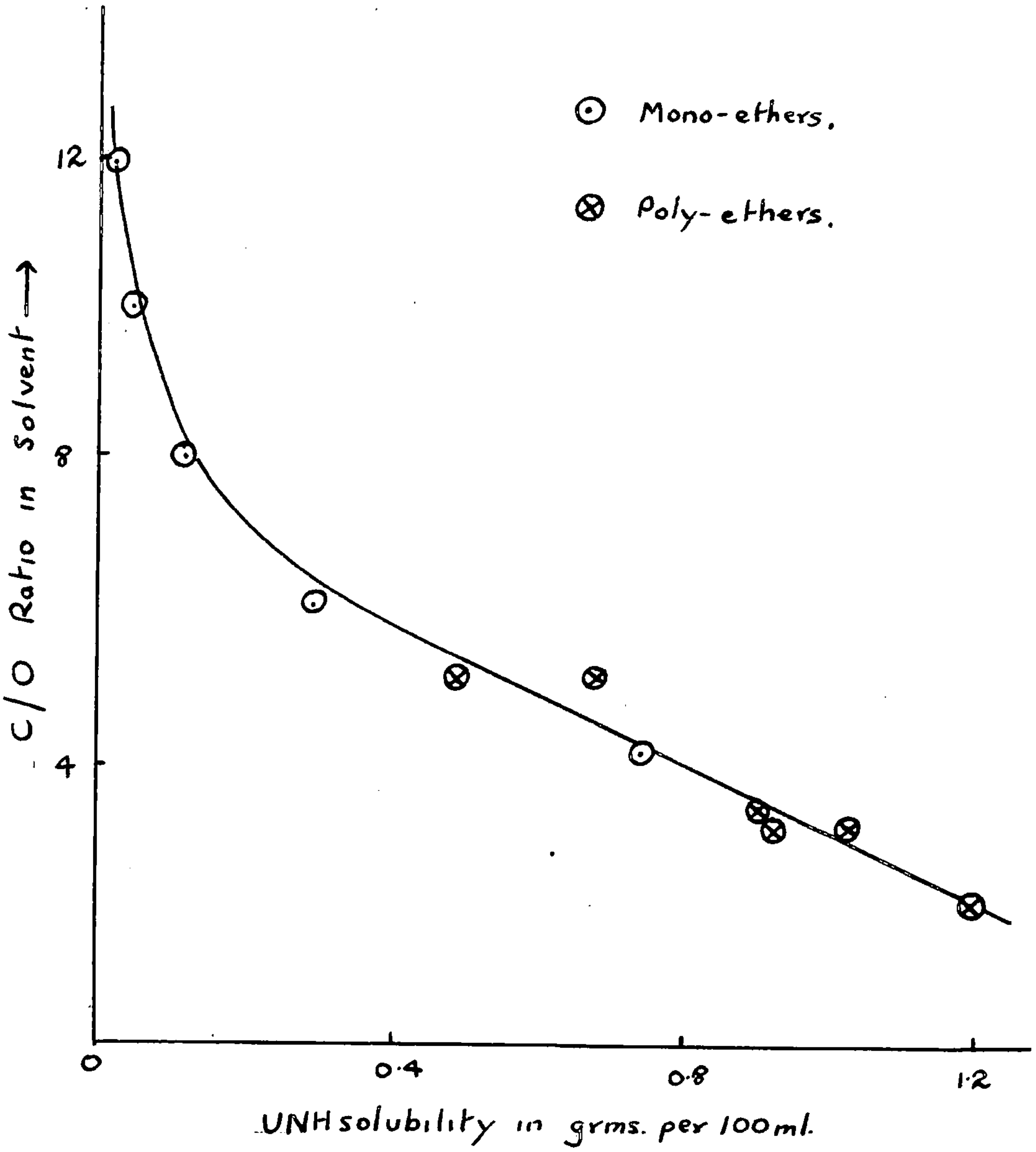


FIG. XXVIII. SOLUBILITY OF URANYL NITRATE IN ALCOHOLS.

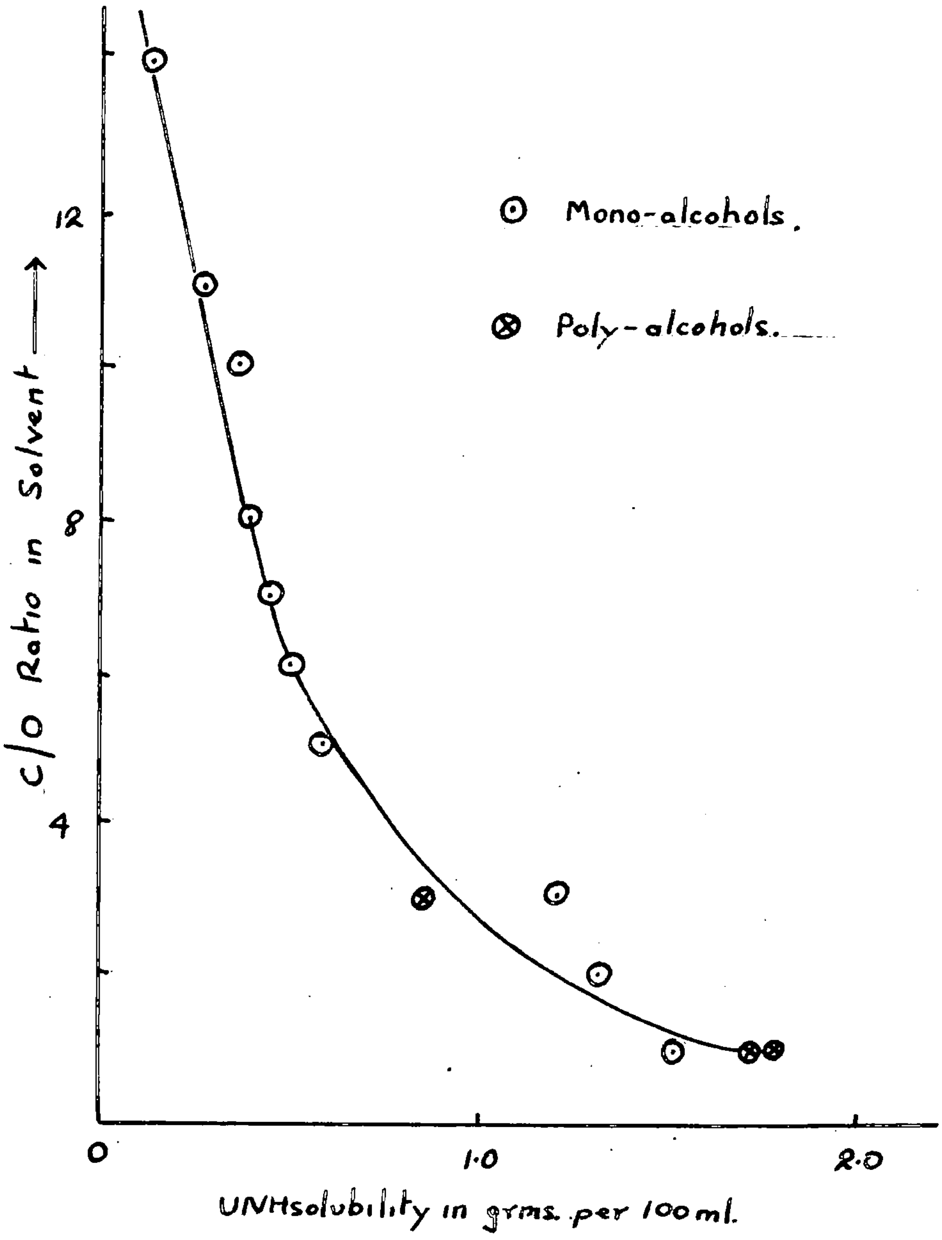
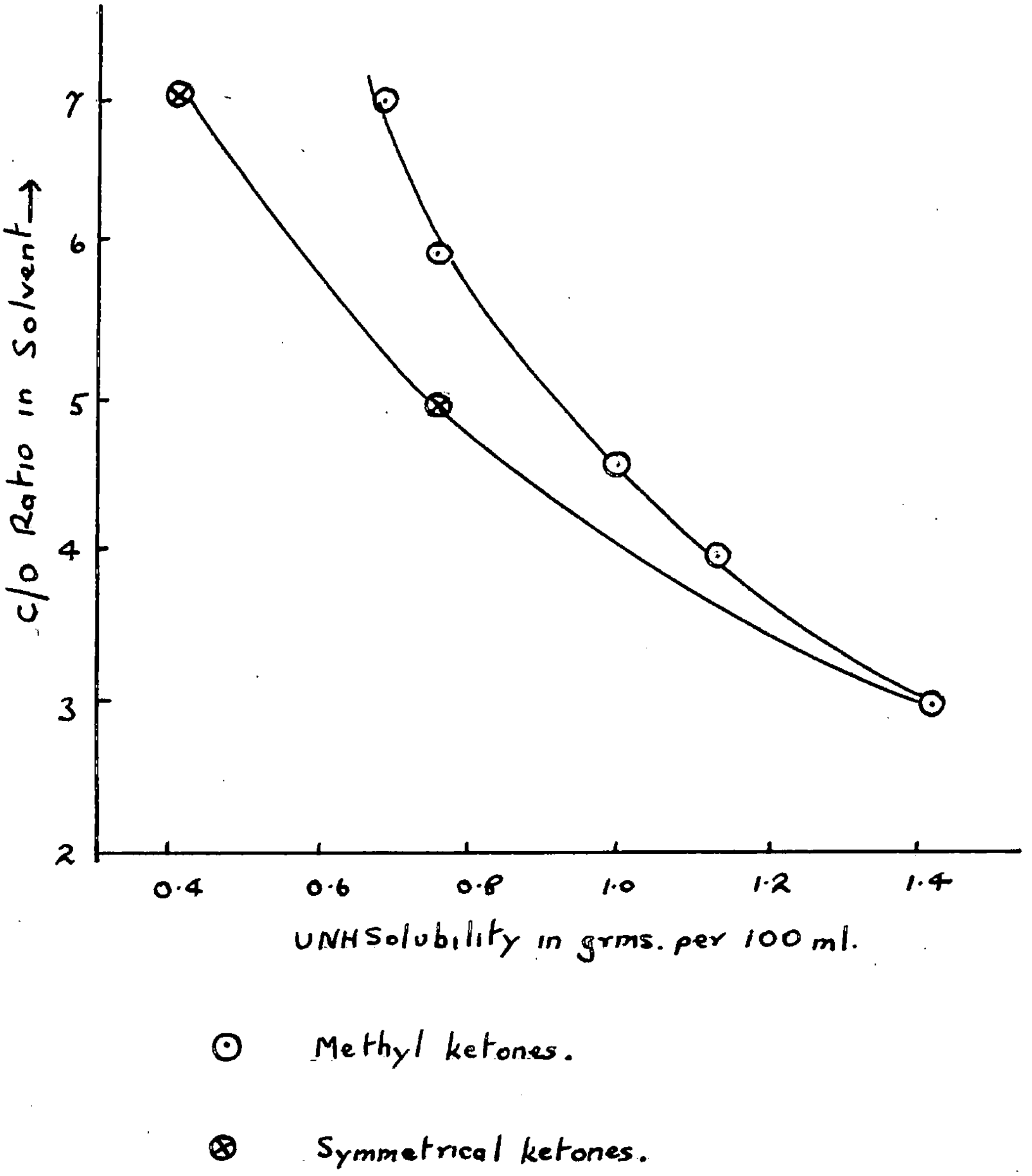


FIG. XXIX. SOLUBILITY OF URANYL NITRATE IN KETONES.



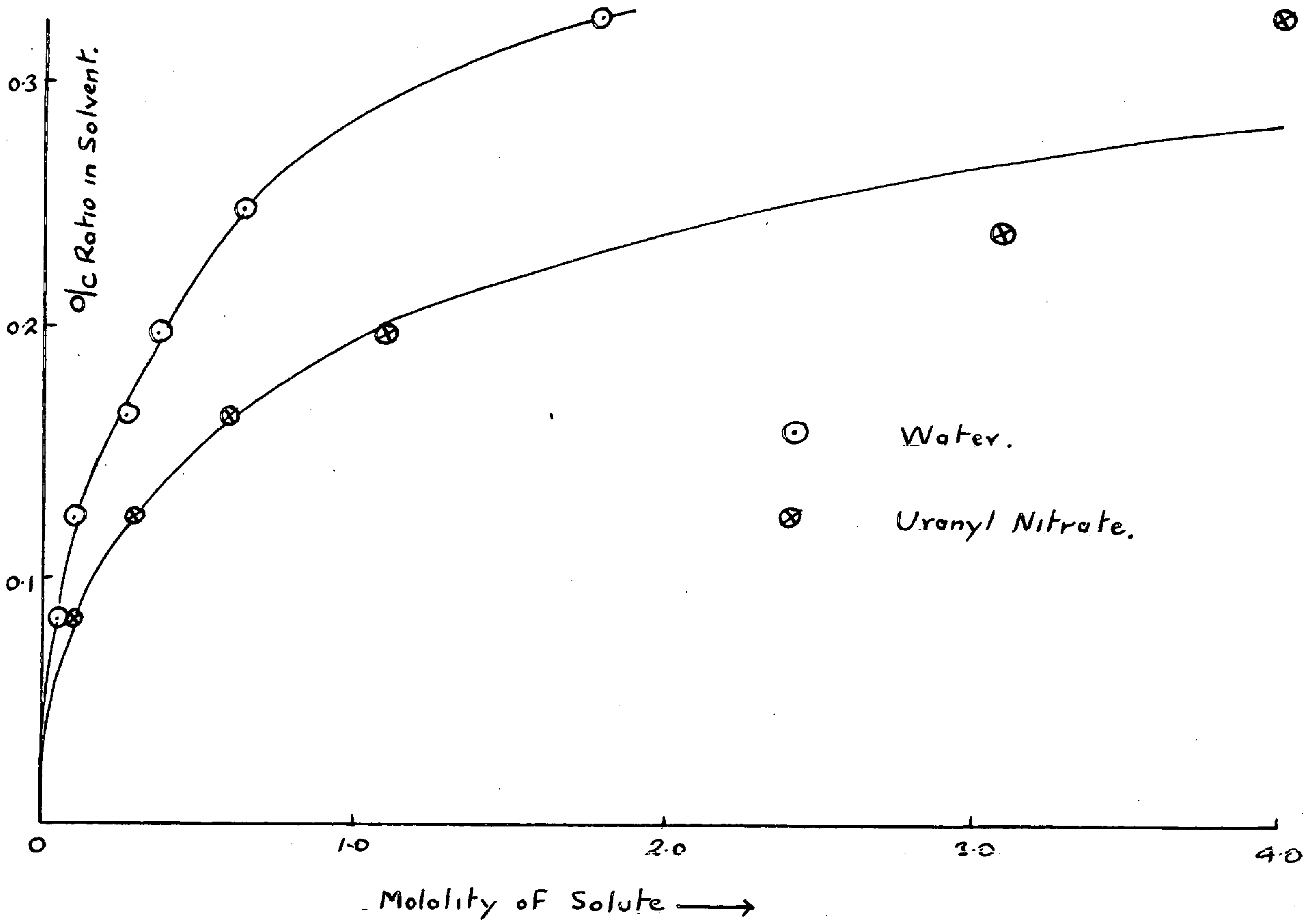


FIG. XXX. SOLUBILITY OF WATER AND URANYL NITRATE IN ETHERS.

Chapter VI. Stability of some solvates of Uranyl Nitrate

Experimental Techniques and the preparation and analysis of the solvates

Preparation of the solvates

Solutions of uranyl nitrate hexahydrate in the solvents were saturated at elevated temperature and allowed to cool. Alternatively a saturated solution was subjected to a current of hot air, which passed over its surface. The resultant crystals were carefully and rapidly dried in a special centrifuge (fig. XXXI) designed for the purpose, and on filter paper. The centrifuge consisted of a metal basket inside which was fitted a roll of filter paper to which the crystals clung. Holes in the walls of the basket allowed the free liquid to be thrown out. The dry crystals were kept in bottles with ground greased stoppers in dark cupboards or a refrigerator, and were used as soon as possible.

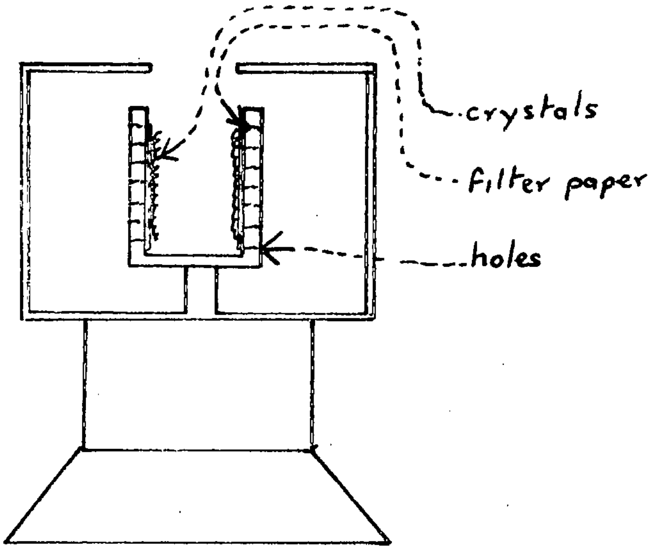


Fig. XXXI

Analyses

The crystals were analysed for uranium by conversion to U_3O_8 and weighing. This could be performed with a reproducibility of ± 0.2%, sufficient to indicate the formula of the crystals, since addition or removal from the molecule of one of its lightest units, a molecule of water, caused a change of approximately 1.6% in the uranium content. A silica crucible, previously heated to 800°C in a furnace, cooled in a desiccator and weighed, was weighed containing a convenient quantity - about 2-3 gms. - of the crystals. The crucible was gently heated on a hotplate, with a current of air blowing over it, until the crystals were converted to the orange oxide. The crucible was then ignited to constant weight in a furnace at 800°C, with open doors to allow free access of air. Each determination was done in duplicate.

Solvent content was determined in a number of cases by pumping off and weighing. A weighed quantity of finely-ground crystals were placed in a vessel (A) connected to a vacuum pump via a second vessel (B) surrounded by liquid air (fig. XXXII) and pumped for a period. Solvent mixed with a little water collected in B and was weighed after removal of the water with anhydrous $CuSO_4$. The residual crystals were shown to be chiefly $UO_2(NO_3)_2 \cdot 3H_2O$.

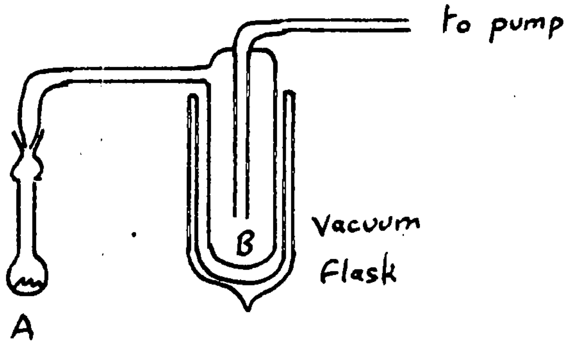


Fig. XXXII

Analyses were performed on the crystals

(i) when freshly prepared
(ii) after exposure to ordinary air for given periods
(iii) after remaining in a desiccator for given periods

to identify the decomposition products.

Results

(i) Crystals from a solution of $UO_2(NO_3)_2.6H_2O$ in methyl ethyl ketone

Freshly prepared crystals:- uranium content (i) 45.8%
(ii) 45.8%
ketone content 13.9%

Formula $UO_2(NO_3)_2.3H_2O.CH_3COC_2H_5$ requires 45.8% uranium
13.85% ketone

Exposure to air:-

Exposed to ordinary air		Exposed to air in a desiccator	
Time of exposure (hours)	% uranium	Time of exposure (hours)	% uranium
0	45.8	0	45.8
1	45.9		
4	46.0		
19	47.1	19	53.0
67	38.6	67	53.1

Table 10.

The uranium and ketone content of the fresh crystals clearly shows their formula to be $UO_2(NO_3)_2.3H_2O.CH_3COC_2H_5$ - a new compound. Exposed to ordinary (wet) air, the uranium content of the crystals rises, presumably due to loss of solvent, as the crystals smelt of ketone. Pick-up of moisture occurred also, resulting finally in wet crystals and a low uranium content. Exposed to dry air in a desiccator, the uranium content of the crystals rose to 53.1%, that of $UO_2(NO_3)_2.3H_2O$. At the same time the crystals collapsed to a powder, and no longer smelt of ketone. All these phenomena are in accord with a formula of $UO_2(NO_3)_2.3H_2O.CH_3COC_2H_5$ for the crystals.

(ii) Crystals from an acetone solution

Freshly prepared crystals:- uranium content (i) 47.0%
(ii) 47.0%
ketone content 11.5%
Formula $UO_2(NO_3)_2.3H_2O.CH_3COC_2H_5$ requires 47.1% uranium
11.47% ketone

Table 11

The formula $UO_2(NO_3)_2.3H_2O.CH_3COCH_3$ is clearly indicated for the crystals which are a new compound, homologous with $UO_2(NO_3)_2.3H_2O.CH_3COC_2H_5$, and analogous with the ether complex $UO_2(NO_3)_2.3H_2O.(C_2H_5)_2O$, prepared by von Unruth[1].

(iii) Crystals from a diethyl ether solution

Freshly prepared crystals:- uranium content (i) 45.27%
(ii) 45.17%
Formula $UO_2(NO_3)_2.3H_2O.(C_2H_5)_2O$ requires 45.6% uranium
Exposure to air:-

Exposed to ordinary air		Exposed to air in a desiccator	
Time of exposure (hours)	% uranium	Time of exposure (hours)	% uranium
0	45.27	0	45.17
1	48.5	1	47.0
4.5	47.7	4.5	49.57
70	47.7	70	53.1

Table 12

The uranium content of the crystals was a little lower than that demanded by the formula, due probably to the crystals being slightly wet with ether. Their extremely labile nature rendered efficient drying impossible. Exposed to ordinary air, the crystals quickly lose ether, and the uranium content rises, falling later as water is picked up. In a desiccator the crystals are converted to $UO_2(NO_3)_2.3H_2O$, shown by a final uranium content of 53.1%, the crystals falling to a powder in the process. All these phenomena are in accord with von Unruth's[1] formula of $UO_2(NO_3)_2.3H_2O.(C_2H_5)_2O$ for the crystals, which is therefore confirmed.

(iv) Crystals from a dibutyl ether solution

Freshly prepared crystals:- uranium content	(i)	47.4%
	(ii)	47.4%
Ether content		0
Formula $UO_2(NO_3)_2.6H_2O$ requires		47.4% uranium.

Table 13

The crystals were $UO_2(NO_3)_2.6H_2O$.

(v) Crystals from a diethyl ketone solution

Freshly prepared crystals:- uranium content	(i)	48.6%
	(ii)	48.5%
	(iii)	48.6%
Exposed to ordinary air:- uranium content		47.5%
Exposed to air in a desiccator:- uranium content		52.9%

Table 14

The uranium content of the freshly prepared crystals does not correspond to any simple formula such as $UO_2(NO_3)_2.3H_2O.C_2H_5COC_2H_5$. However, an equimolecular mixture of $UO_2(NO_3)_2.3H_2O.C_2H_5COC_2H_5$ and

$UO_2(NO_3)_2 \cdot 3H_2O$ would have a uranium content of 48.8%. This would explain the conversion of the crystals to trihydrate in a desiccator.

(vi) Crystals from a methyl isobutyl ketone solution

Freshly prepared crystals: - uranium content	(i)	48.18%
	(ii)	48.22%
Exposed to air in a desiccator:- uranium content		53.0%

Table 15

A formula of $UO_2(NO_3)_2 \cdot CH_3COC_4H_9$ has a uranium content of 48.2%, but this would not explain the formation of trihydrate in the desiccator, and such a compound is unlikely because no compound of uranyl nitrate having less than two solvates has previously been prepared. An equimolecular mixture of $UO_2(NO_3)_2 \cdot 3H_2O \cdot CH_3COC_4H_9$ and $UO_2(NO_3)_2 \cdot 3H_2O$ is a more likely explanation, having also a uranium content of 48.2%, and explaining the formation of trihydrate in the desiccator.

(vii) Crystals from a di-isopropyl ether solution

Freshly prepared crystals:- uranium content	(i)	32.34%
	(ii)	32.61%
Exposed to air in a desiccator:- uranium content		52.9%

Table 16

No simple formula can explain these results.

Conclusions

Complexes of uranyl nitrate with the solvent may generally be crystallised from solutions of uranyl nitrate hexahydrate in ethers and ketones. The formula for the diethyl ether complex is the same as that of one of the ether complexes of Katzin and Sullivan[2], and von Unruth[1], and the result for dibutyl ether is in accordance with Katzin and Sullivan's[2] work, but the ketone results differ. Katzin and Sullivan[2] have mixtures of $UO_2(NO_3)_2.3H_2O$ and $UO_2(NO_3)_2.2H_2O.S$ for acetone and methyl isobutyl ketone, but no $UO_2(NO_3)_2.3H_2O.S$. Their results do not necessarily preclude the existance of such compounds however. Vapour pressure determinations to be described also support the formula $UO_2(NO_3)_2.3H_2O.S$, and the conversion of the compounds to $UO_2(NO_3)_2.3H_2O$ in a desiccator, shown in several instances, supports this formula also.

The extreme lability of the complexes is evident in their spontaneous decomposition in air. The solvent molecules are obviously much more weakly bonded than are the water molecules.

Sufficient complexes have now been prepared, in this research, and by Katzin[3], and Katzin and Sullivan[2], to show that the phenomenon is a general one, common to most organic uranyl nitrate solutions.

Quantitative estimate of the stability of the solvates

The stability of the solvent complexes of uranyl nitrate has been shown qualitatively to be low, but the result needs putting on a more quantitative footing. The method used also demonstrates that the complexes are true compounds.

Theoretical

Consider the complex $UO_2(NO_3)_2.3H_2O.S$ crystallising from solution in vacuo, with progressive removal of the vapour phase. The following equilibria will be set up:-

$$
\begin{array}{llll}
1) & \text{Saturated Solution}_l \rightleftharpoons & UO_2(NO_3)_2 \cdot 3H_2O \cdot S_s & + \; S_g \\
2) & UO_2(NO_3)_2 \cdot 3H_2O \cdot S_s \rightleftharpoons & UO_2(NO_3)_2 \cdot 3H_2O_s & + \; S_g \\
 & & \quad\quad \upharpoonleft\downharpoonright & \\
 & & UO_2(NO_3)_2 \cdot 2H_2O_s & + \; H_2O_g \\
3) & UO_2(NO_3)_2 \cdot 3H_2O_s \rightleftharpoons & UO_2(NO_3)_2 \cdot 2H_2O_s & + \; H_2O_g
\end{array}
$$

(subscripts refer to solid, liquid, gas)

If the vapour pressure of the system were followed, it should show three 'steps' in its descent. A curve of vapour pressure against quantity of vapour removed from the system should have the form shown in Fig. XXXIII. If such curves were obtained

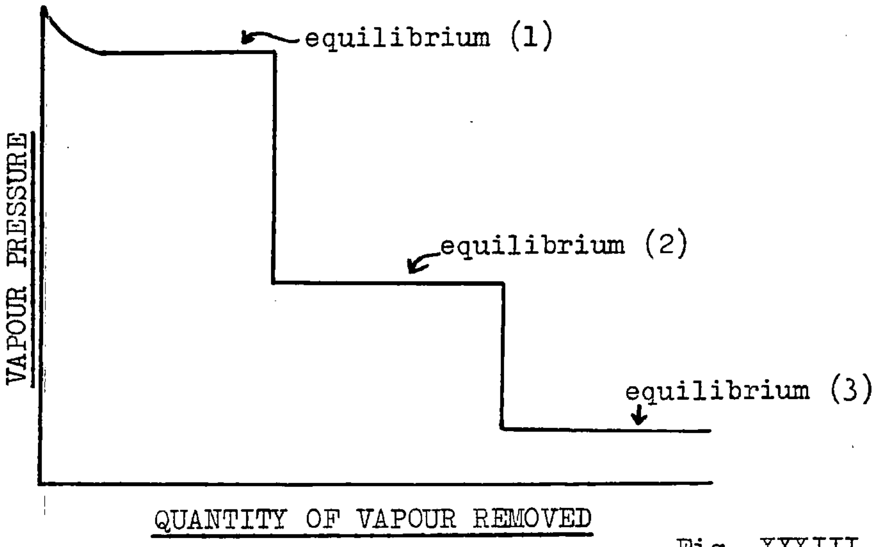


Fig. XXXIII

for two different temperatures, and the partial pressures P_1 and P_2 of the solvent at temperatures T_1 and T_2 at the second equilibrium were inserted in the equation

$$
\mathrm{Log}_{10} \frac{P_1}{P_2} = \frac{-\Delta H}{4.573} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \qquad (1)
$$

then ΔH, which represents the heat of the decomposition reaction

$$UO_2(NO_3)_2.3H_2O.S_s \rightleftharpoons UO_2(NO_3)_2.3H_2O_s + S_g - Q_A \qquad (A)$$

could be calculated. The heat of this reaction (Q_A) gives a measure of the energy of rupture of the solvent - uranyl nitrate bond.

Measurement of the vapour pressures of the system described will therefore allow an estimate of the strength of the solvent - uranyl nitrate bond to be made. The following additional information can also be obtained:-

(i) The existence of three 'steps' in the vapour pressure curve would prove conclusively that the crystals described in the previous section represent a true compound of uranyl nitrate with its solvent.

(ii) The sharpness of the descents between the steps would show whether the various solid phases enter into solid solutions with one another.

(iii) If the final step could be identified with the trihydrate independently, then the formula $UO_2(NO_3)_2.3H_2O.S$ for the complex receives further confirmation.

(iv) The heat Q_B of the reaction

$$UO_2(NO_3)_2.6H_2O_s + S_g \rightleftharpoons UO_2(NO_3)_2.3H_2O.S_s + 3H_2O_g + Q_B \qquad (B)$$

represents the energy relationship between the hexahydrate and the complex in the presence of their vapours. It may by calculated from the equations

$$UO_2(NO_3)_2.3H_2O_s + S_g \rightleftharpoons UO_2(NO_3)_2.3H_2O.S_s + Q_A$$

$$UO_2(NO_3)_2.6H_2O_s \rightleftharpoons UO_2(NO_3)_2.3H_2O_s + 3H_2O_g - 35.79 \text{ K-cal.}$$

(de Forcrand[4])

Experimental

Apparatus. The system described was investigated using the apparatus shown in Fig. XXXIV, for the solvents acetone, methyl ethyl ketone, diethyl ketone, and diethyl ether. A manometer of large bore ($\frac{3}{4}$") containing mercury was viewed through a cathetometer one meter away. Behind the manometer stood a large box (G) containing two electric light bulbs, and the side of the box facing the manometer was made of opal glass. An adjustable strip of black glass (H) was held horizontally behind, and just above, the mercury meniscus, to give it a sharp edge for reading. Each limb of the manometer was closed by a tap, and connected to bulbs B and C. Beyond another pair of taps the two limbs were joined and connected through a tap to the system A. The apparatus was designed so that, using only bulb B as solution-container, vapour from the solution could fill the apparatus as far as D. The vapour filling the system A (between taps D and J) could then be pumped off, and fresh vapour from the solution allowed to refill it. In this way vapour from the solution could be removed and the vapour pressure of the system measured after each removal. The bulb A could be replaced by bulbs of different sizes. The apparatus was connected to a vacuum system at E, the trap K serving to prevent vapour contaminating the pump.

Testing. The accuracy of the apparatus was tested by measuring the vapour pressures of saturated solutions of NaCl and KCl at 25°C, and comparing the results with published data. Bulb B (Fig. IV) contained the saturated solution (with excess of solid present), and bulb C glass-distilled water. The apparatus was thoroughly evacuated, making use of charcoal and liquid air (F) and the liquids boiled and the apparatus re-evacuated several times. Bulbs B and C were then surrounded by a constant temperature bath, well-stirred, at 25°C, after bulb B had been heated to about 26° to ensure complete saturation at 25°. The vapour pressure of

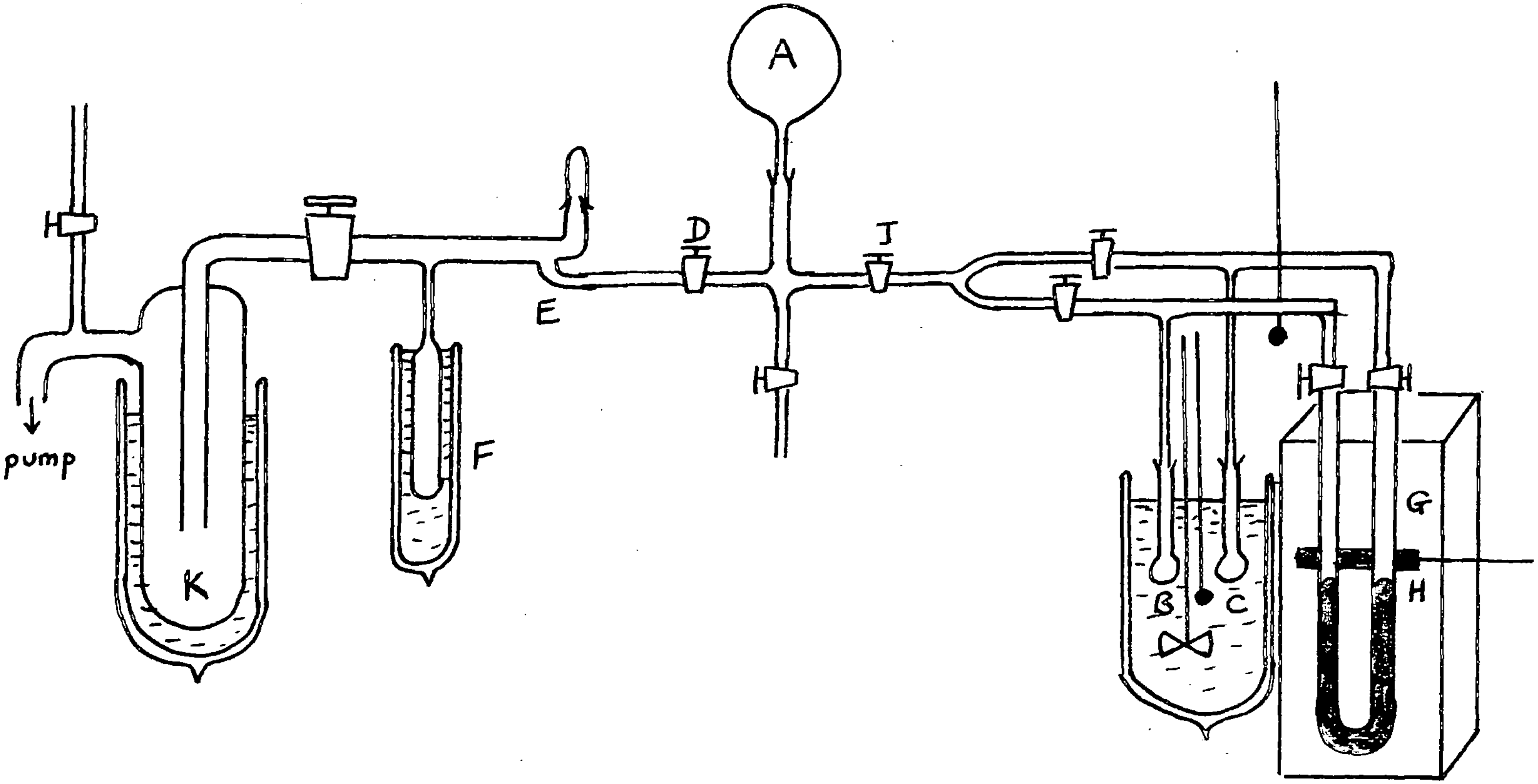


Fig. XXXIV

the solution, and the difference between that of the solution and of pure water, were both read. The results are shown in Table 17, together with literature values[5].

Comparison of measured and literature vapour pressures

NaCl	25°	KCl	25°
Vapour Pressure measured	17.893 mm	Vapour Pressure measured	20.233
Vapour Pressure from literature	17.924	Vapour Pressure from literature	20.260
Water activity measured	0.7532	Water activity measured	0.8517
Water activity from literature	0.7545	Water activity from literature	0.8528

Table 17

The Stability Experiments. The bulb B contained the solutions, the other arm of the manometer being closed after the apparatus had been thoroughly evacuated. Bulb B was surrounded by the constant temperature bath, and vapour from the solution was allowed to fill the apparatus as far as D. Before a reading of the vapour pressure could be taken, equilibrium conditions had to be attained, and though this was facilitated by soaking the solution on to cotton wool, thereby exposing a greater area, at least 24 hours were necessary for equilibrium to be reached. The vapour contained in A was repeatedly abstracted, allowing curves of vapour pressure against quantity of vapour removed to be plotted. The following solutions were examined:-

(i) $UO_2(NO_3)_2.3H_2O.CH_3COCH_3$ in acetone at 0° and 12°

(ii) $UO_2(NO_3)_2.6H_2O$ in acetone at 19°

(iii) $UO_2(NO_3)_2.3H_2O.CH_3COC_2H_5$ in methyl ethyl ketone at 0° and 12°

(iv) The diethyl ketone complex in diethyl ketone at 15°, 20°, 25°

(v) $UO_2(NO_3)_2.3H_2O.(C_2H_5)_2O$ in diethyl ether at 0°

Results

Figs. XXXV to XXXVIII show the results, plotted as vapour pressure against quantity of vapour removed. In figs. XXXV and XXXVI the first flat portion represents the equilibrium vapour pressure of the saturated solution. When only solid complex remains, further removal of vapour results in a sharp reduction of pressure, and a new level is formed, representing the equilibrium pressure of a mixture of complex, trihydrate and dihydrate. When all the solvent has been pumped off, a new pressure drop occurs to a level representing the water-vapour pressure of the trihydrate-dihydrate equilibrium. The sharp drop from one plateau to the next shows that, for acetone and methyl ethyl ketone, the phase change does not involve solid solutions of the complex with the trihydrate. In the case of diethyl ketone (fig. XXXVII) the steps are much less sharp, though clearly recognisable, but in the case of diethyl ether there are no well-defined plateaux observable. A summary of the vapour pressures is given in Table 18, together with the calculated heats of reactions A and B.

The values of Q_A shown in the table suggest that the bonds holding the ketone molecules to the uranyl nitrate are very weak, perhaps similar to hydrogen bonds or little more than van der Waals forces. This is consistent with the labile nature of the crystals. The heat of formation of the trihydrate from the dihydrate can be calculated from the vapour pressure curve, 12.53 K-cals. per mol. H_2O removed. The most reliable existing data[6], calculated from heats of solution measured by de Forcrand[4], gives 13.36 K-cals.

Vapour Pressures of the Complexes

Complexing Solvent	Temp. °C	Vap. Press. of Sat.Soln. mm.	Vap.Press.of Complex-trihy-dihyd. equl^m.	Water vapour press. of trihyd-dihyd. equlm.	Q_A Kg/cal	Q_A Kg/cal
Acetone	0.0	22.75	6.61	1.25		
	6.0				8.49	
	9.5				8.53	
	12.0	29.50	13.60	3.28		-27.29
	15.5				8.58	
	19.0	43.00	21.00	5.79		
Methyl Ethyl Ketone	0.0	15.80	4.37	1.25		
	6.0				9.84	
	12.0	21.18	9.98	3.28		-26.34
Diethyl Ketone	15.0	-	5.75	4.16		-21.79
	17.5				14.05	
	20.0	-	8.60	6.30	14.18	
	22.5				14.30	
	25.0	-	12.80	9.50		

Table 18

per mol. Values of Q_B, shown in the last column of Table 18, indicate that reaction B,

$$UO_2(NO_3)_2.6H_2O_s + S_g \rightleftharpoons UO_2(NO_3)_2.3H_2O.S_s + 3H_2O_g + Q_B$$

is endothermic, in the sequence acetone > methyl ethyl ketone > diethyl ketone, the reverse order of the stability of the complexes.

References to Chapter VI

1. von Unruth, Dissert. Rostock., 1909-1913.
2. Katzin and Sullivan, Atomic Energy Commission Declassified Report AECD 2537
3. Katzin, AECD 2213
4. de Forcrand, Compt.Rend. 1913, 156, 1044-1048.
   Ann.Chim. 1915, 3[9], 22.
5. Robinson and Stokes, Trans.Farad.Soc., 1949, 45, 612.
6. Gmelins Handbuch der Anorganische Chemie.

FIG XXXV. ACETONE SOLUTIONS.

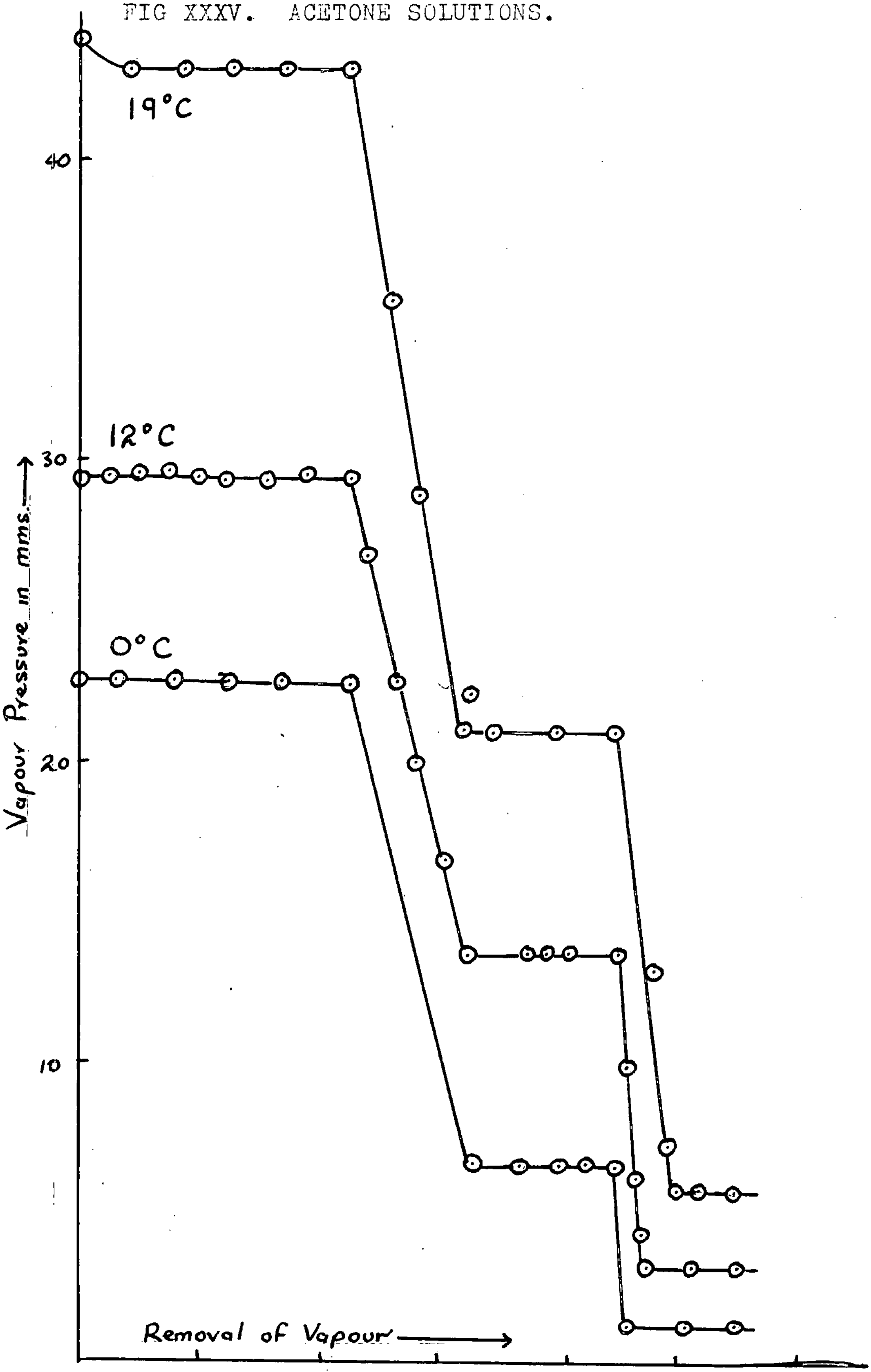


FIG.XXXVI. METHYL ETHYL KETONE SOLUTIONS.

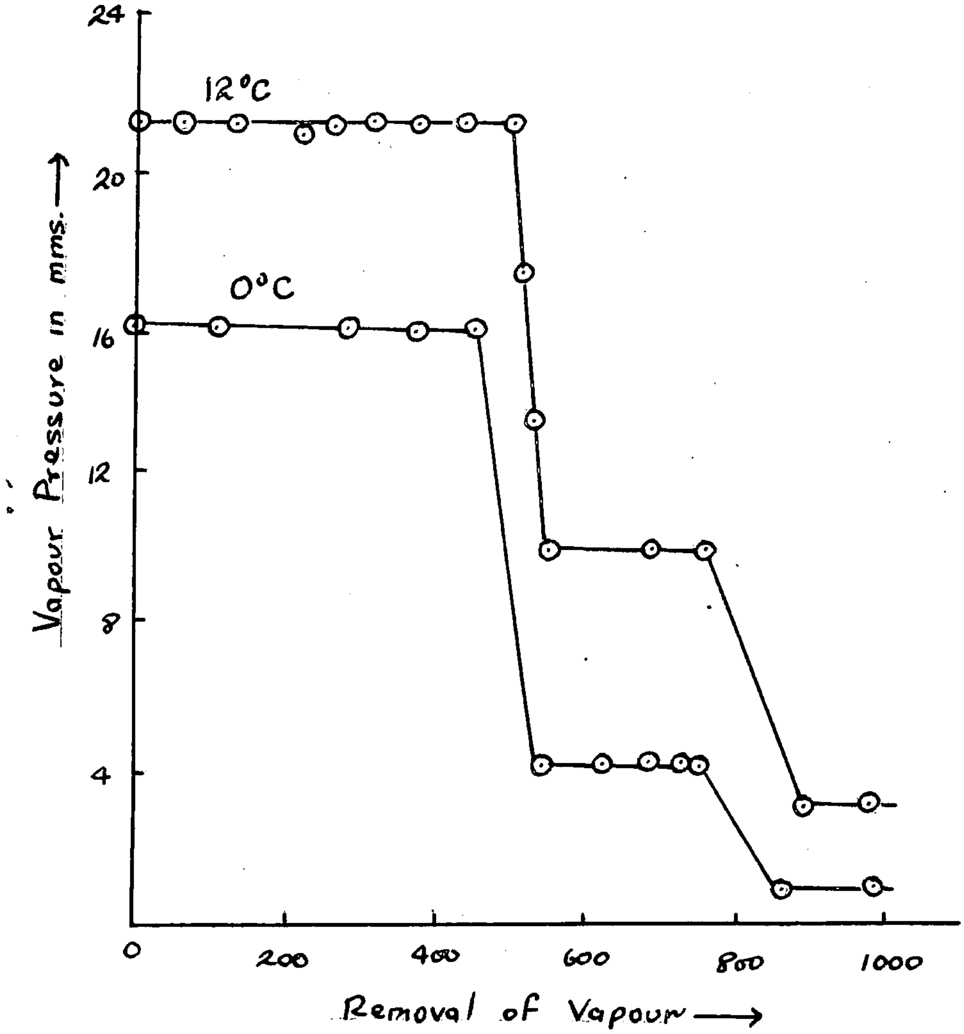


FIG.XXXVII. DIETHYL KETONE SOLUTIONS.

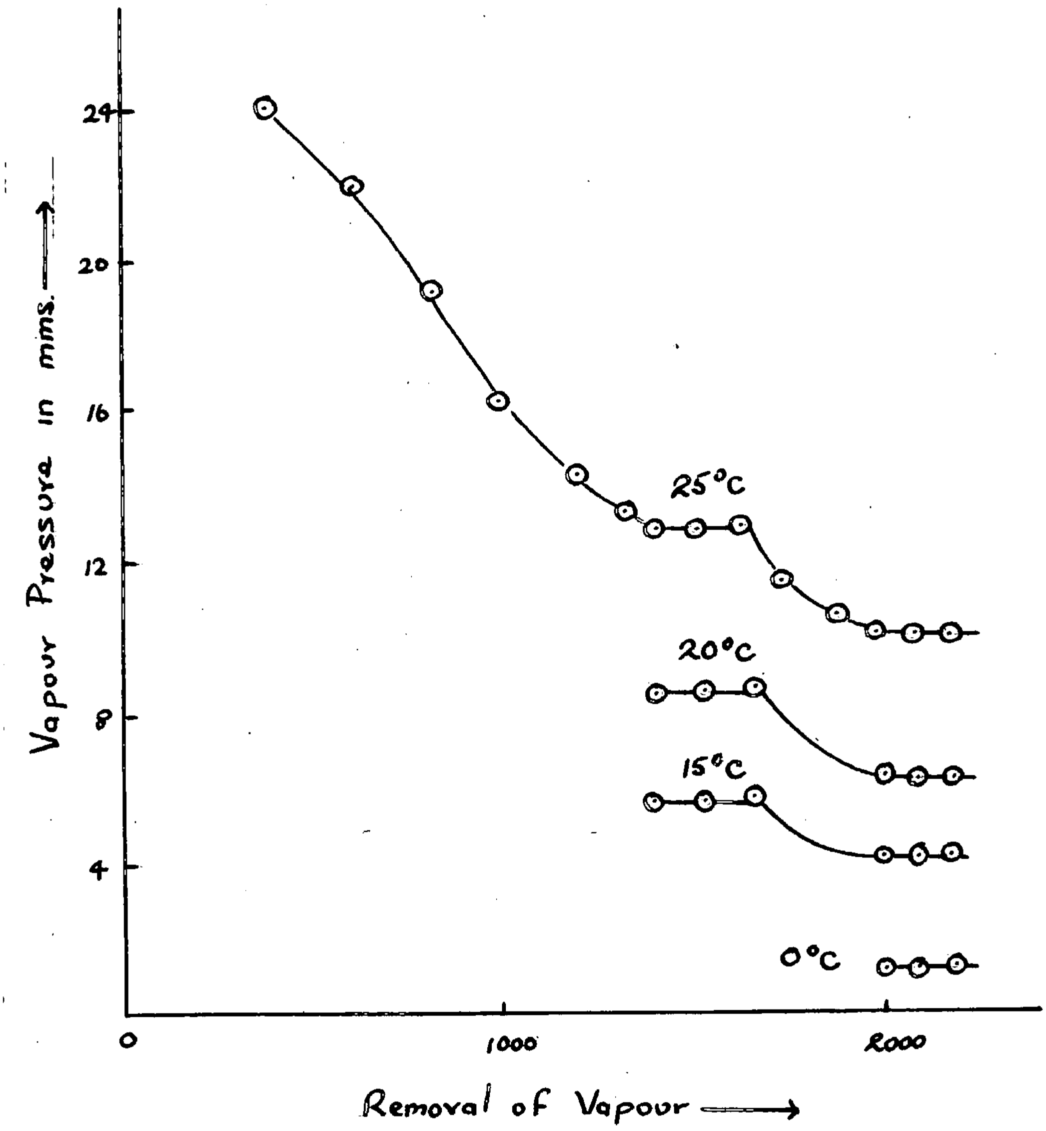
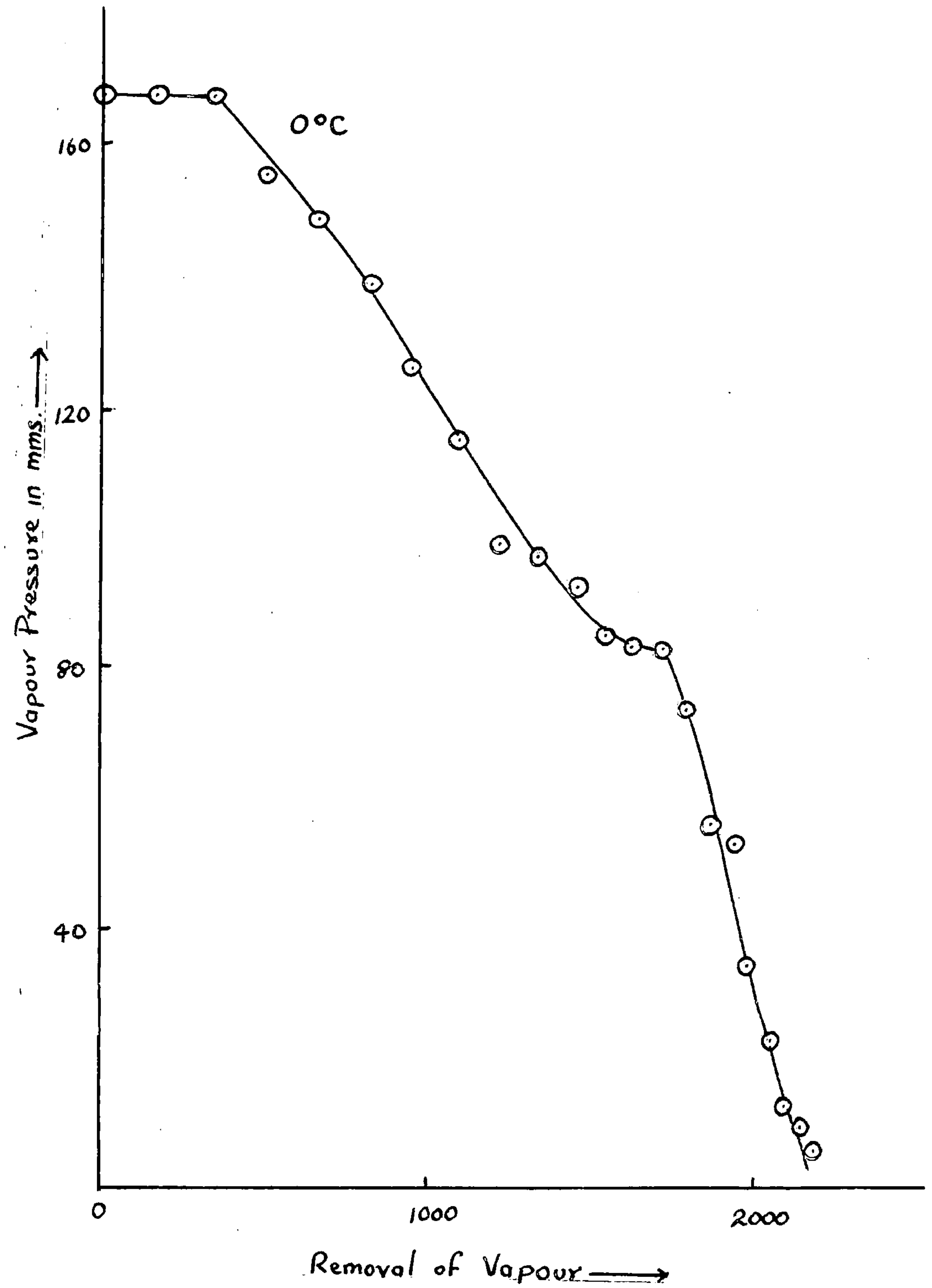


FIG.XXXVIII. DIETHYL ETHER SOLUTIONS.



Chapter VII. Constitution of the Organic Uranyl Nitrate Solutions

Although the detailed constitution of the organic uranyl nitrate solutions has been somewhat extensively treated from a thermodynamic standpoint in Chapter V, at this stage a qualitative pictorial summary of the conclusions established there will probably be of some value.

Such a qualitative over-all picture, by its very nature, will be an approximation. In particular solvents, and under particular conditions, alterations in it will be necessary. In particular, the picture will not be applicable to alcoholic solutions except in the very broadest general sense. To those solutions in which uranyl nitrate is associated with four molecules of water, the picture can only apply if it is assumed that the uranyl nitrate exists as a tetrahydrate. This may not be so, the solutions may contain a mixture of different hydrates which is usually stoichiometrically equal to a tetrahydrate. No evidence exists on this point.

In the organic solutions the four water molecules and the two nitrate groups will be assumed to be attached to the uranyl group by primary valence forces, possibly coordinate in nature. The hydrogen atoms belonging to the four attached water molecules will then be free to form hydrogen bonds with the oxygen atoms of the solvent. A molecule of uranyl nitrate dissolved in ether would then appear somewhat like the picture shown in fig. XXXIX. Probably not all the hydrogen atoms would form hydrogen bonds with the solvent, as the results in Chapter V show, though they would all be available.

This rough picture explains satisfactorily most of the experimental facts, e.g.

(1) Dominant role of the oxygen atom in the solvents.

(2) Solutions are almost completely unionised

(3) Effect of electron-attracting substituents in the solvents.

(4) Uranyl nitrate is more soluble in the organic solvents in the presence, than it is in the absence, of water. As the water content of the solution is reduced, water molecules in the complex would probably be replaced by solvent molecules without the same tendency to form hydrogen bonds.

(5) Uranyl nitrate is more soluble in the solvents, mole for mole, than is water. The water molecules in the complex will probably be electron-deficient if they are united to the uranyl radical by coordinate valency forces, and this will enable the hydrogen atoms more readily to form hydrogen bonds with the solvent.

(6) Methyl alcohol, glycol, and glycerol are better solvents than is water. Hydrogen-bonded solvents are better donor solvents[1] and so should show greater solubility for $UO_2(NO_3)_2.4H_2O$. In water itself however the solubility is probably reduced by the very high degree of association of the molecules.

(7) The fact that methyl ethyl ketone + 15% xylene behaves normally is in agreement with these conclusions.

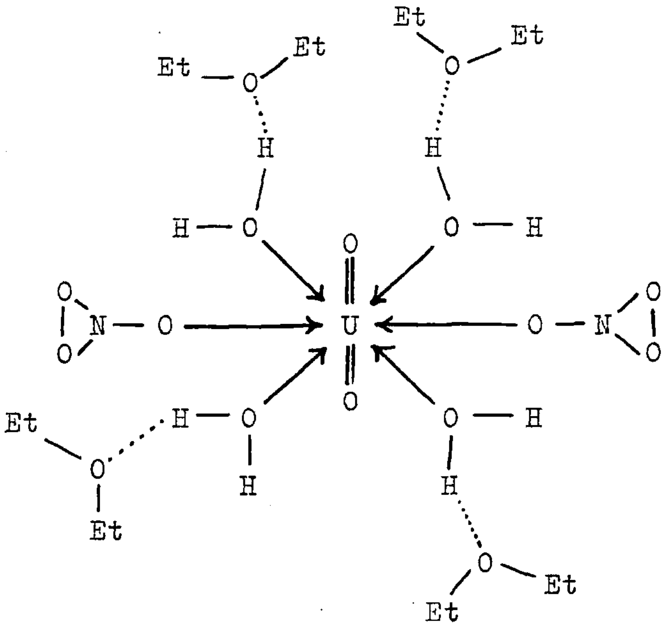


Fig. XXXIX

The solubility relations discussed at the end of Chapter V are in general agreement with the picture, and may be explained either by steric considerations or by electron drifts.

Proton-attracting Power

The overall picture may be co-related with some experiments on proton-attracting power. From studies by infra-red spectroscopy, of the strength of hydrogen bond formation with heavy methanol, Gordy and Stanford[2] established the order of proton attracting power for a number of types of solvents:-

alcohols > ethers > ketones

diethyl ether > higher ethers

Diethyl ether > dioxane

acetone > methyl isobutyl ketone

diethyl ether > methyl isobutyl ketone.

These relationships are true also for the solubility of uranyl nitrate in the solvents, except insofar as the relationships between ketones and the other solvent types are considered. If the structurally similar aldehydes are made to replace the ketones in the inequalities previously listed, then they apply without qualification to the solubility of uranyl nitrate in the solvents. Chapter V shows that aldehydes should show greater uranyl nitrate solubility than ketones, but in practice the reverse is the case. It may be, therefore, that the ketones behave anomalously in this respect.

Non-conducting uranyl nitrate solutions

Jander and Wendt[3] have discovered another non-conducting uranyl nitrate solution - that of anhydrous uranyl nitrate in 100% nitric acid. Potassium nitrate dissolved in this solvent is a strong electrolyte. They also have prepared 99.2% $UO_2(NO_3)_2$.

References to Chapter VII

1. Zellhoeffer, Copley and Marvel, J.Amer.Chem.Soc., 1940, 62, 227.
2. Gordy and Stanford, J.Chem.Phys., 1940, 8, 170.
3. Jander and Wendt, Z.Anorg.Chem., 1949, 258, 1-14.

Appendix I. The water content of organic uranyl nitrate solutions

A. Diethyl ether solutions

The "phase volume" method was used throughout, 50 mls. of water being taken, except that the first point is, of course, always determined by water titration.

Water content of diethyl ether uranyl nitrate solutions

wt.UNH taken g	Vol.aq. layer (mls)	Vol.org. layer (mls)	wt.UN (org) g.	wt.H_2O (org) g.	wt.ether (org.) g.	Molality UN (org)	Molality H_2O (org)
0	0	0	0			0	0.65
5.000	0.10	49.7	3.882	0.985	37.06	0.266	1.475
10.000	0.40	49.9	7.653	1.802	37.03	0.524	2.701
15.000	0.80	51.0	11.34	2.510	37.00	0.777	3.76
20.000	1.29	51.86	14.95	3.170	36.96	1.026	4.76
25.000	1.72	53.35	18.55	3.891	36.93	1.273	5.84
30.000	2.20	53.47	22.08	4.566	36.90	1.516	6.87
35.000	2.90	54.79	25.40	5.084	36.84	1.749	7.46
40.000	3.40	56.57	28.77	6.126	36.80	1.984	9.22
45.000	4.10	57.20	31.95	6.322	36.75	2.206	9.56
50.000	4.75	57.62	35.11	6.908	36.70	2.428	10.45
55.000	6.30	58.50	37.31	6.778	36.59	2.588	10.29

B. Di-isopropyl ether solutions

The "phase volume" method was used throughout, 50 ml. of ether being taken. In this and the following tables the middle columns of the previous table will be omitted for the sake of brevity, leaving only the experimental results and the calculated molalities.

Water content of di-isopropyl ether uranyl nitrate solutions

Wt. UNH taken (g)	Vol. aq. layer	Vol. org. layer	Molality UN	Molality H_2O
0	-	-	0	0.26
5.000	0.26	49.94	0.259	1.31
7.500	0.51	49.99	0.381	1.84
10.000	0.84	50.67	0.495	2.26
12.000	1.23	51.17	0.576	2.46
14.000	1.44	51.13	0.670	2.87

C. Dibutyl ether solutions

The "phase volume" method was used, 50 ml. of ether being taken.

Water content of dibutyl ether uranyl nitrate solutions

Wt. UNH taken (g)	Vol. aq. layer	Vol. org. layer	Molality UN	Molality H_2O
0	-	-	0	0.094
1.0004	0.04	49.78	0.0501	0.268
2.0012	0.13	49.70	0.0960	0.478
3.0012	0.22	49.61	0.1424	0.704
4.0015	0.33	49.42	0.1874	0.833
5.0002	0.55	51.15	0.228	0.833

D. $\beta\beta'$ dibutoxyethyl ether solutions

The phase volume method was used, 50 mls. of solvent being taken, but the method of mixing was used for the last point.

Water content of dibutyl diethylene glycol solutions

Wt. UNH added	Vol. aq. layer	Vol. org. layer	Molality UN	Molality H_2O
0			0	0.760
5.000	0.28	51.07	0.217	1.100*
5.000	0.23	50.35	0.217	1.085*
10.000	0.64	52.41	0.426	2.193
10.000	0.35	52.45	0.426	2.310
15.000	0.84	53.31	0.642	3.429
20.000	1.20	54.75	0.849	4.574
25.012	2.95	54.50	0.992	4.846
25.000	1.80	57.55	1.087	4.856
5.000	0	50.00	0.220	1.550

* shown to be low ∵ equilibrium only reached slowly. On prolonged shaking all aq. phase dissolved, and extra water dissolved also, bringing m_{H_2O} up to 1.550.

E. ββ' dibutoxyethoxyethyl ether solutions

The first three points were obtained by water titration, and the subsequent ones by the phase volume method.

Wt. UNH added	Vol. solvent taken	Vol. H_2O added	Molality UN	Molality H_2O
0	50.00		0	2.25
10.000	50.00	1.37	0.426	4.18
20.000	50.00	0.60	0.852	5.83
	Vol. aq. layer	Vol. org. layer		
30.000	0.30	56.60	1.272	7.36
40.000	1.70	59.80	1.65	8.48
50.000	3.30	60.30	1.993	9.53
60.000	5.20	59.00	2.279	10.46

F. β-ethoxyethyl ether solutions

The first seven points were done by water titration and the last two by the phase volume method.

Water content of diethyl cellosolve uranyl nitrate solutions

Wt. UNH added	Vol. solvent taken (ml.)	Vol. H_2O added (ml)	Molality UN	Molality H_2O
0	50.0	1.86	0	2.44
5.000	50.0	1.80	0.234	3.77
10.000	50.0	1.65	0.468	4.99
15.000	50.0	1.55	0.702	6.25
20.000	50.0	1.50	0.936	7.61
30.000	50.0	1.30	1.408	10.15
40.000	50.0	1.40	1.876	13.14
	Vol. aq. layer	Vol. org. layer		
12.000	0.08	10.0	2.80	16.6
12.000	0.45	8.0	3.40	18.6

G. Isoamyl acetate solutions

The "phase volume" method was used, 50 ml. of ester being taken.

Water content of isoamyl acetate uranyl nitrate solutions

Wt. UNH added	Vol. aq. layer	Vol. org. layer	Molality UN	Molality H_2O
0	-	-	0	0.44
5.000	0.18	51.27	0.222	1.174
10.000	0.60	52.50	0.432	2.097
15.000	1.50	53.55	0.618	2.536
20.000	2.80	54.05	0.780	2.569
25.000	3.00	55.85	0.986	3.785
30.000	3.80	57.95	1.162	4.374
35.000	4.75	57.45	1.323	4.942

H. Isobutyl alcohol solutions

The first seven points were obtained by water titration, and the last two by the mixing technique.

Water content of isobutyl alcohol uranyl nitrate solutions

Wt. UNH taken	Vol. solvent taken	Vol. H_2O added	Molality UN	Molality H_2O
0	30.0	5.07	0	11.50
3.000	30.0	4.37	0.244	11.37
6.000	30.0	4.43	0.488	12.97
12.000	30.0	4.11	0.976	15.17
18.000	30.0	3.22	1.464	16.08
24.000	30.0	2.50	1.951	17.37
30.000	30.0	1.70	2.439	18.50
UNH present	Aq. layer separating	Total volume		
1.500	0.47	50.0	0.122	11.12
2.500	1.00	106.0	0.048	10.93

J. Isoamyl alcohol solutions

The first five points were obtained by water titration, the next four by phase volumes, and the last three by the mixing method.

Water content of isoamyl alcohol uranyl nitrate solutions

Wt. UNH taken	Vol. solvent taken	Vol. H_2O added	Molality UN	Molality H_2O
0	50.0		0	5.53
5.000	50.0	2.75	0.246	5.24
10.000	50.0	2.30	0.492	6.08
15.000	50.0	1.43	0.738	6.35
20.000	50.0	0.56	0.984	6.64
	Vol. aq. layer	Vol. org. layer		
25.000	0.03	58.27	1.225	7.32
30.000	0.72	59.46	1.435	8.01
35.000	1.75	60.25	1.625	8.41
40.000	2.85	61.38	1.795	8.90
UNH present	Aq. layer separating	Total volume		
12.500	0.00	50.0	0.62	6.43
7.095	0.09	20.0	0.90	6.92
5.000	0.25	104.3	0.151	5.27

K. Secondary octyl alcohol solutions

The first six points were obtained by the phase volume method and the last by mixing.

Wt. UNH taken	Vol. aq. layer	Vol. org. layer	Molality UN	Molality H_2O
0			0	1.85
5.000	0.10	50.00	0.239	1.34
10.000	0.30	53.35	0.482	2.57
15.000	1.15	53.60	0.680	3.08
20.000	2.20	54.45	0.864	3.44
25.000	3.15	55.20	1.038	3.92
UNH present	Aq.layer separating	Total volume		
5.000	0.10	50.00	0.239	1.34

L. Methyl ethyl ketone solutions

All the points were obtained by water titration.

Wt. UNH taken	Vol. solvent taken	Vol. H_2O added	Molality UN	Molality H_2O
0	50.0	6.05	0	8.34
5.000	50.0	5.33	0.247	8.84
5.000	50.0	5.36	0.247	8.80
15.000	50.0	5.62	0.742	12.20
25.000	50.0	5.75	1.237	15.34
35.000	50.0	5.18	1.731	17.52
50.000	50.0	4.87	2.47	21.52
60.000	50.0	4.45	2.97	23.92
70.000	50.0	4.64	3.46	27.14
80.000	50.0	7.00	3.96	33.36
90.000	50.0	8.12	4.45	37.87
100.000	50.0	9.70	4.95	43.06

M. Methyl isobutyl ketone solutions

All the points were obtained using the phase volume method.

Wt. UNH taken	Vol. aq. layer	Vol. org. layer	Molality UN	Molality H_2O
0	-	-	0	1.225
5.001	0.10	49.99	0.246	1.367
10.002	0.36	52.24	0.486	2.454
15.003	0.41	53.87	0.730	3.980
20.005	0.74	54.96	0.963	5.10
25.005	1.10	56.83	1.191	6.20
30.005	1.78	56.49	1.400	6.95
35.007	2.80	58.53	1.587	7.34
40.000	3.50	59.45	1.786	8.10
45.000	4.30	60.05	1.957	8.86
50.000	5.00	60.15	2.140	9.57

N. Cyclohexanone solutions

The first five points were obtained by water titration, and the last two by the phase volume method.

Wt. UNH taken	Vol. solvent taken	Vol. H_2O added	Molality UN	Molality H_2O
0	50.0	3.07	0	3.599
10.003	50.0	2.37	0.420	5.320
20.003	50.0	1.70	0.841	7.037
30.000	50.0	0.54	1.146	8.295
40.003	50.0	0.17	1.682	10.290
	Vol. aq. layer	Vol. org. layer		
60.000	1.65	70.25	2.465	13.57
80.000	3.80	75.80	3.190	16.72

All the water solubilities recorded agree quite well with literature values from the handbooks except that of methyl ethyl ketone, which is high. This is presumably due to some water-miscible impurity, such as alcohol. Acetone was shown to be absent, and so was alcohol.

Appendix II

Partition of Uranyl Nitrate between water and organic solvents

1. Di-isopropyl ether (by R. Jenkins)

Aqueous Phase	Molality	2.51	2.12		1.339
	density	1.625	1.566	1.467	1.374
Organic Phase	Molality	0.303	0.144		0.0135
	density	0.8032	0.7602	0.7272	0.7260

2. β-butoxyethyl butyl ether (by R. Jenkins and M. Rigg)

Aqueous Phase	Molality	2.25	1.60	1.045	0.746	0.557	0.519
	density	1.599	1.466	1.320	1.225	1.173	1.166
Organic Phase	Molality	0.641	0.187	0.0337	0.00512	0.00264	0.00214
	density	1.012	0.8940	0.8374	0.833	0.833	0.833

3. ββ' dibutoxydiethyl ether (by R. Jenkins and A.R. Mathieson)

Aqueous Phase	Molality	1.70	1.36	1.03	0.580	0.119
	density	1.470	1.400	1.313	1.180	1.040
Organic Phase	Molality	1.26	0.767	0.318	0.0468	0.00030
	density	1.131	1.079	0.974	0.900	0.883

4. ββ'-dibutoxyethoxyethyl ether (by A.R. Mathieson)

Aqueous Phase	Molality	3.181	2.002	1.343	0.765	0.396	0.260
	density	1.781	1.526	1.387	1.231	1.133	1.077
Organic Phase	Molality	3.078	2.156	1.066	0.630	0.153	0.0476
	density	1.398	1.338	1.244	1.096	0.9853	0.9529

5. Dibutyl ether (by A.R. Mathieson, V. Mitchell and M. Rigg)

Aqueous Phase	Molality	3.16	2.85	2.74	2.59	2.56	2.46	2.17
	density	1.785	1.718					
Organic Phase	Molality	0.288	0.173	0.144	0.0975	0.1105	0.0641	0.0302
	density	1.038	0.807	0.800	0.794	0.795	0.782	0.779
Aqueous Phase	Molality	2.02	2.02	1.87	1.71	1.56	1.43	1.21
	density							
Organic Phase	Molality	0.0208	0.0212	0.0157	0.0093	0.0059	0.0040	0.0027
	density	0.771	0.771	0.765	0.760	0.765	0.765	0.765

6. Isoamyl acetate (by M. Rigg)

Aqueous Phase	Molality	3.16	2.00	1.55	1.090	0.699	0.523
	density	1.79	1.54	1.44	1.310	1.203	1.150
Organic Phase	Molality	1.218	0.348	0.131	0.0249	0.00369	0.00150
	density	1.17	0.960	0.902	0.876	0.869	0.868

7. Isoamyl alcohol (by M. Rigg)

Aqueous Phase	Molality	3.24	2.06	1.53	0.913	0.490
	density	1.770	1.533	1.409	1.277	1.139
Organic Phase	Molality	1.92	0.965	0.513	0.136	0.0128
	density	1.240	1.049	0.931	0.845	0.818

8. Secondary Octyl Alcohol (by M.G. Beadle and E.S. Busk)

Aqueous Phase	Molality	3.14	2.522	1.922	1.738	1.332	1.120	1.077	0.8761
	density	1.799	1.669	1.531		1.383		1.315	
Organic Phase	Molality	1.00	0.714	0.374	0.289	0.100	0.0524	0.0427	0.0167
	density	1.079	1.004	0.928		0.854		0.839	

9. Methyl ethyl ketone (by A.R. Mathieson)

Aqueous Phase	Moles/lit.	2.060	1.953	1.843	1.723	1.577	1.445	1.324	1.218	1.112	0.4275	0.3275	0.2100
Organic Phase	Moles/lit.	2.485	2.320	2.162	1.990	1.778	1.487	1.433	1.290	1.152	0.2210	0.1074	0.03145

10. Cyclohexanone (by A.R. Mathieson)

Aqueous Phase	Molality	3.21	2.304	1.378	1.346	0.851	0.382	0.208
	density	1.804	1.616	1.396	1.312	1.232	1.122	1.058
	Molality	3.675	2.514	1.443	1.354	0.668	0.1673	0.0353
	density	1.610	1.462	1.284	1.213	1.125	1.003	0.9568