

### S 59. Stability of Complexes of Uranyl Nitrate with Ketones and Ethers.

By A. R. MATHIESON.

New complexes of uranyl nitrate with ketones have been prepared by dissolving  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in the ketones, and subsequent crystallisation. Those formed by acetone and methyl ethyl ketone were shown by analysis to have the formula  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{X}$  (X = ketone). The vapour-pressure curves of evaporating solutions of the complexes in their own ketone as solvent, determined at different temperatures, enabled the energies of rupture of the ketone-uranyl nitrate bonds to be estimated. The formation by diethyl ether of a complex  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot (\text{C}_2\text{H}_5)_2\text{O}$  was confirmed, and related compounds appear to be formed by  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with some ketones. The absorption spectra of organic solutions of the complexes were compared with that of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in water. The bearing of these results on the solubility of uranyl nitrate in the solvents under consideration is discussed.

URANYL nitrate is soluble in a large range of organic solvents, most readily in alcohols, esters, ketones, ethers, and other oxygen-containing solvents. Uranyl salts are known to form many complexes with organic molecules (von Unruth, Diss., Rostock, 1909, 58; Rascanu, *Ann. sci. Univ. Jassy*, 1930—1933, 17, 131; Asahina and Dono, *Z. physiol. Chem.*, 1930, 186, 133; Montignie, *Bull. Soc. chim.*, 1934, [v], 1, 410; Pace, *Arch. Farm. speriment.*, 1926, 42, 39). Uranyl nitrate will also form complexes with some of its solvents, such complexes having been reported by von Unruth (*loc. cit.*), who claimed to have prepared, by evaporation in dry air or *in vacuo* of the ethereal layer of a solution of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in ether, a complex  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot (\text{C}_2\text{H}_5)_2\text{O}$ , and a further complex  $\text{UO}_2(\text{NO}_3)_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$  from a solution of  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in ether. From the system uranyl nitrate-ammonia-ether he claimed to have isolated four complexes,  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NH}_3$ ,  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NH}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ ,  $\text{UO}_2(\text{NO}_3)_2 \cdot 4\text{NH}_3$ , and  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{NH}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ . More recently, Chantrel (Diplome d'Etude sup., Rennes, 1948) prepared a number of such organic compounds of uranyl nitrate, including one with dioxan, and he considers it possible that hydrogen bonding might give rise to such organic complexes.

The possibility of preparing these complexes by the method used by von Unruth was investigated, and the formation of two new compounds (i) *uranyl nitrate-acetone trihydrate*,  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{COMe}_2$  (m. p. 57°), and (ii) *uranyl nitrate-butan-2-one trihydrate*,  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{COMeEt}$  (m. p. 61°), was established by analysis. The stability of these compounds was assessed (a) by allowing them to decompose under various conditions, and (b) from the energy of rupture of the solvent-uranyl nitrate bonds, as determined from the vapour-pressure curves of evaporating solutions of the compounds. The heats of solution of  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and of  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{COMeEt}$  in methyl ethyl ketone were measured and compared with those calculated from the vapour pressures, and the absorption spectra of some organic solutions of uranyl nitrate were compared with that of its aqueous solution.

The behaviour of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with ketones and ethers was also investigated to discover if any parallelism exists with the uranyl analogue. Cobalt nitrate was found to give a trihydrated complex with methyl ethyl ketone.

## EXPERIMENTAL.

*Materials.*—Uranyl nitrate hexahydrate was of "AnalaR" quality. The following solvents were purified by distillation: acetone, methyl ethyl ketone, diethyl ketone, methyl *isobutyl* ketone, diethyl ether, *diisopropyl* ether, dibutyl ether.

*Preparation of Complexes.*—Solutions of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in the solvents saturated at elevated temperature were allowed to cool. The resultant crystals were carefully and rapidly dried in a centrifuge and on filter-paper, more extensive drying being impossible owing to their labile nature.

*Analysis.*—The complexes were analysed for uranium by conversion into  $\text{U}_3\text{O}_8$  and weighing. This could be performed with a reproducibility of  $\pm 0.2\%$ , sufficient to indicate the formula of the complex, 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. Ketone content was determined by pumping off the volatile material and weighing the residue. *Uranyl nitrate-acetone trihydrate* [Found: U, 47.0; acetone, 11.5.  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{C}_3\text{H}_6\text{O}$  requires U, 47.1; acetone, 11.5%]. *Uranyl nitrate-butan-2-one trihydrate* [Found: U, 45.8;  $\text{C}_4\text{H}_8\text{O}$ , 13.9.  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{C}_4\text{H}_8\text{O}$  requires U, 45.8;  $\text{C}_4\text{H}_8\text{O}$ , 13.85%]. *Uranyl nitrate-diethyl ether trihydrate* [Found: U, 45.2. Calc. for  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{C}_4\text{H}_{10}\text{O}$ : U, 45.6%]. Analyses were also performed after exposure to dry air and to ordinary air for fixed times, to identify the decomposition products.

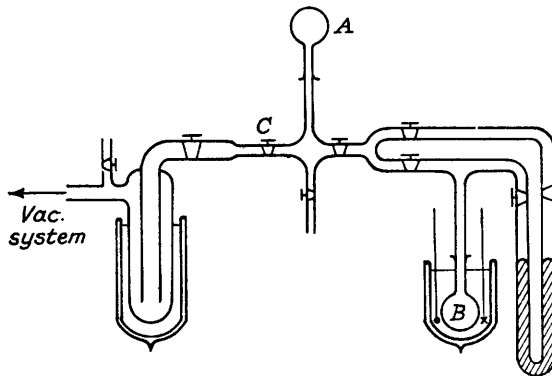
The following table shows the results of analyses of the crystals obtained from solutions of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in acetone, methyl ethyl ketone, ethyl ether, and dibutyl ether. The last does not form a complex under the experimental conditions. Diethyl ketone, methyl *isobutyl* ketone,

*Analyses of solvent complexes of uranyl nitrate.*

Complexing solvent.	Treatment.	Formula proposed.	U, %.		Solvent, %.	
			Found.	Calc.	Found.	Calc.
Acetone	Drying	$\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{COMe}_2$	47.0	47.1	11.5	11.47
Methyl ethyl ketone	Drying	$\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{COMeEt}$	45.8	45.8	13.9	13.85
	Exposed to dry air	$\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	53.1	53.1	0	0
Diethyl ether	Drying	$\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{Et}_2\text{O}$	45.2	45.6	—	—
	Exposed to dry air	$\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	53.1	53.1	—	—
Dibutyl ether	Drying	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	47.4	47.4	0	0

and *diisopropyl* ether appeared to form complexes, but the analyses did not indicate their formulæ unambiguously, and further investigation is necessary. All the complexes and uranyl nitrate hexahydrate revert to uranyl nitrate trihydrate when left in a desiccator for more than 24 hours. Exposed to ordinary air, the three complexes in the above table first lose their solvent, as shown by an increase in the uranium content, and then absorb moisture until they approximate to  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

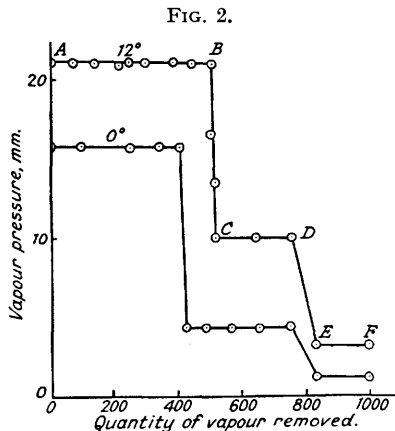
FIG. 1.

*Vapour-pressure apparatus.*

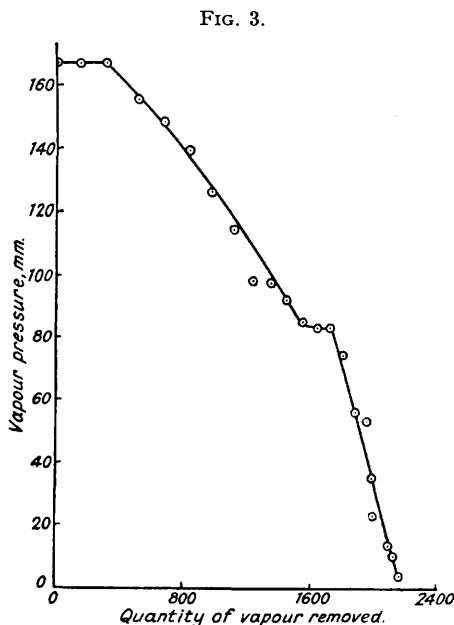
*Stability of the Complexes.*—*Vapour-pressure data.* The vapour-pressure curves of the evaporating solutions of uranyl nitrate in the solvents were determined by using the apparatus shown in Fig. 1, which enabled part of the volume of vapour over the solution to be removed repeatedly, the solution replacing it by evaporation, and the vapour pressure to be read before each removal. The bulb (A), which contained most of the vapour to be removed, was replaceable by bulbs of different volume. The bulb (B), which contained the solution, was frozen in liquid air while the whole apparatus was thoroughly evacuated. One arm of the manometer was then closed, the liquid air removed and replaced by a Dewar vessel containing water at a fixed temperature, and vapour from the solution allowed to fill the apparatus as far as (C). Before a reading of the vapour pressure could be made, 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, and a reading of the vapour pressure taken each time,

allowing curves of vapour pressure against quantity of vapour removed to be plotted. The following solutions were examined: (i)  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in acetone at  $19^\circ$ ; (ii)  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{COMe}_2$  in acetone at  $0^\circ$  and  $12^\circ$ ; (iii)  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{COMeEt}$  in methyl ethyl ketone at  $0^\circ$  and  $12^\circ$  (Fig. 2); (iv) the diethyl ketone complex in the ketone at  $15^\circ$ ,  $20^\circ$ , and  $25^\circ$ ; (v)  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{Et}_2\text{O}$  in ether at  $0^\circ$  (Fig. 3).

Fig. 2 shows the plot of vapour pressure against the quantity of vapour removed for the methyl ethyl ketone complex. The first flat portion ( $A-B$ ) represents the equilibrium vapour pressure of the saturated solution. When only solid complex remains, further removal of vapour results in a sharp



Vapour-pressure curves of uranyl nitrate-methyl ethyl ketone.



Vapour-pressure curve of uranyl nitrate-ether at  $0^\circ$ .

reduction of pressure, and a new level ( $C-D$ ) 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 fall occurs, to a level representing the water-vapour pressure of the trihydrate-dihydrate equilibrium ( $E-F$ ). The sharp fall from one plateau to the next shows that the phase change does not involve solid solutions of the complex with the trihydrate.

Similar curves are obtained for the acetone complex. The steps for the diethyl ketone complex are much less sharp, though clearly recognisable, but with the ether complex there are no well-defined plateaux observable (Fig. 3). A summary of the vapour pressures is given in the following table.

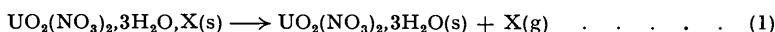
Equilibrium vapour pressures and thermal data for ketone complexes of uranyl nitrate.

Complexing solvent.	Temp.	Ketone v.p. of satd. soln., mm.	Ketone v.p. of complex, mm.	Water v.p. of trihydrate, mm.	Energy of rupture of U-X bond ( $Q_a$ ), kcals.	Heat of reaction $B$ ( $Q_b$ ), kcals.
Acetone	0.0°	21.50	5.36	1.25	—	—
	6.0	—	—	—	8.49	—
	9.5	—	—	—	8.53	—
	12.0	26.22	10.32	3.28	—	-27.29
	15.5	—	—	—	8.58	—
Methyl ethyl ketone	19.0	37.21	15.21	5.79	—	—
	0.0	14.55	3.12	1.25	—	—
	6.0	—	—	—	9.84	—
Diethyl ketone	12.0	17.90	6.70	3.28	—	-26.34
	15.0	—	1.59	4.16	—	-21.79
	17.5	—	—	—	14.05	—
	20.0	—	2.30	6.30	14.18	—
	22.5	—	—	—	14.30	—
	25.0	—	3.30	9.50	—	—

Energies of rupture of the uranyl nitrate-ketone bonds can be calculated from the vapour pressures by means of the equation

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

(where  $P_1$  and  $P_2$  are the partial pressures of ketone at  $T_1^\circ$  and  $T_2^\circ$ , respectively), and are the heats of the reactions:



where X represents one mol. of ketone. The magnitude of these energies suggests that the bonds holding the ketone molecules are van der Waals forces, consistent with the labile nature of the crystals. The energies of bond rupture shown in this table include the heats of evaporation of the ketones.

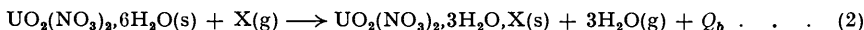
A logarithmic plot of the total vapour pressures of the complexes and of the trihydrate, against temperature, shows that the curves are of the usual type.

The heat of formation of the trihydrate from the dihydrate can be calculated from the vapour-pressure curve of the former, 12.53 kcals. per mole of  $\text{H}_2\text{O}$  being added. The most reliable existing data (Gmelin's "Handbuch"), calculated from heats of solution measured by de Forcrand (*Compt. rend.*, 1913, **156**, 1207; *Ann. Chim.*, 1915, [ix], **3**, 25), give 13.36 kcals. per mole.

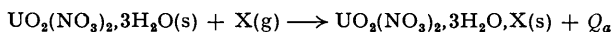
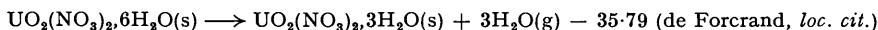
*Heats of solution.* The heat of solution of  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{COMeEt}$  in the ketone, calculated from its solubility in the latter (3.24 g./g. at  $6^\circ$ ) and the vapour-pressure data, is -12.2 kcals. per mole. Measured calorimetrically it is -1.30 kcals. per mole. It would appear from this that the process of crystallisation of the complex from its saturated solution in the ketone takes place in more than one step, only the first of which affects the vapour-pressure measurements.

The heat of solution of uranyl nitrate trihydrate in methyl ethyl ketone was found to be 3.05 kcals. per mole, by calorimetric measurement.

*Heat relationships between the complexes and  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .* In addition to giving a measure of the strength of the ketone-uranyl nitrate bonds, the vapour pressures will also yield the heat relationships between the complexes and the hexahydrate in the presence of their decomposition products:



$Q_b$  may be calculated from the equations



The values of  $Q_b$  for three solvents are shown in the foregoing table, and the reaction is seen to be endothermic in the sequence acetone > methyl ethyl ketone > diethyl ketone, the reverse order of the stability of the complexes.

*Absorption-spectra Measurements.*—The absorption spectra of the following solutions were measured by means of a spectrophotometer: (i)  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{COMe}_2$  in acetone; (ii)  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{COMeEt}$  in the ketone; (iii)  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{Et}_2\text{O}$  in the ether; (iv)  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in water. Fig. 4 shows plots of wave-length ( $m\mu$ .) against extinction coefficient for the four solutions. It is seen that the peaks for the three organic solutions are higher than those of the aqueous solution and are shifted towards the ultra-violet.

*Behaviour of Cobalt Nitrate.*—The behaviour of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with ketones and ethers was cursorily investigated to discover if it was analogous in any way to that of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . It is insoluble in ethers, but soluble in the ketones, though to a markedly smaller extent.

Attempts to prepare complexes from the solutions in the same way as the uranyl complexes were unsuccessful, so saturated solutions of the hydrated salt in the four ketones were treated with xylene until precipitation was complete. The precipitates were dried by centrifugation, filter-paper, and treatment with chloroform. Addition of xylene to the solutions produced the following phenomena:

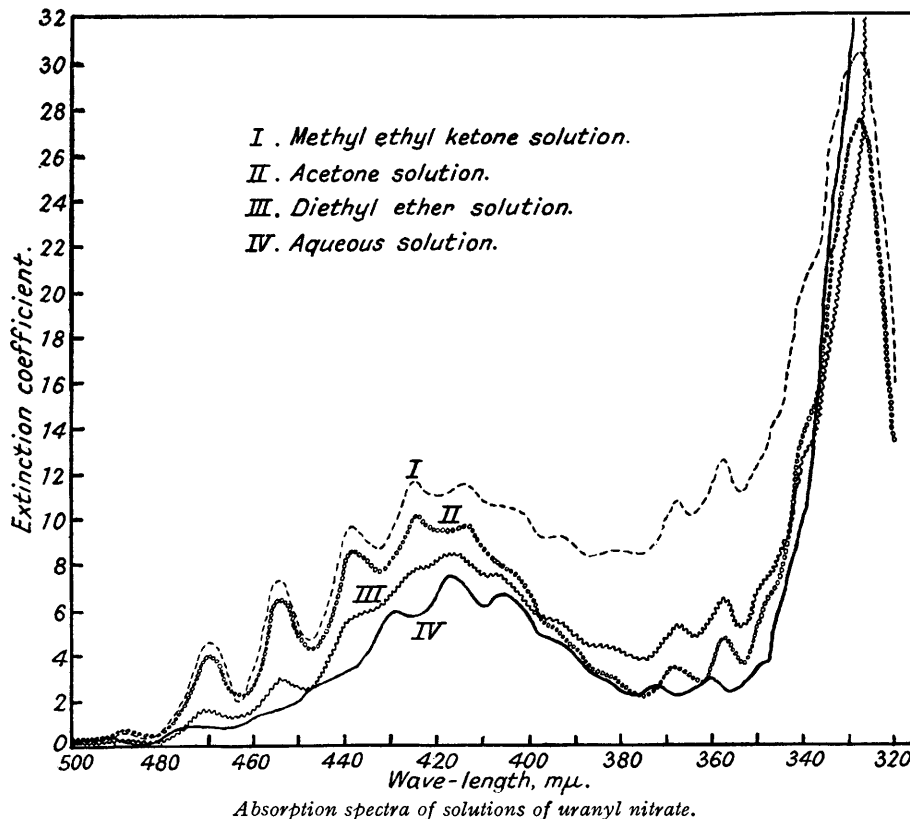
*Acetone.* A lower layer of dark red, apparently supersaturated liquid appeared which slowly crystallised in large orange-pink crystals of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

*Methyl ethyl ketone.* Similar treatment produced apparently colourless flakes seen on drying to be orange-pink and of waxy consistency [Found: Co,  $19.10 \pm 0.01$ .  $\text{Co}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{C}_4\text{H}_8\text{O}$  requires Co, 19.1%], totally unlike  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . Analysis was by conversion into the black oxide mixture, thence into the sulphate by sulphuric and sulphurous acid at  $400^\circ$ , and baking at  $550\text{--}700^\circ$  to constant weight.

*Methyl isobutyl ketone.* A fresh solution produced pale orange-pink flakes, exactly like the preceding ones, but a 2-day-old solution gave a pale grey-green powder. Two different substances seem to be formed here.

*Diethyl ketone.* The precipitate was grey-green like that obtained from the foregoing 2-day-old solution.

FIG. 4.



*Conclusions.*—Complexes crystallise directly from solutions of uranyl nitrate hexahydrate in the solvents, and as their stability is of the same order as that of uranyl nitrate trihydrate, it may be that this complex formation is a principal cause of the solubility of uranyl nitrate in the solvents. This view is supported by the fact that dibutyl ether, which forms no complex under the conditions examined, will dissolve uranyl nitrate only sparingly. The fact that dibutyl ether will dissolve some uranyl nitrate shows that complex formation cannot be the only factor operating, and this is supported by the work of Misciattelli (*Gazzetta*, 1930, **60**, 839) and Guempel (*Bull. Soc. chim. Belg.*, 1929, **38**, 449), who found that ether will dissolve much more uranyl nitrate when saturated with water than when dry, and that uranyl nitrate has a considerable "salting-in" effect on the mutual solubilities of ether and water, generally the case with a solute soluble in both liquids. There is also some evidence to show that complexes between uranyl nitrate and the solvents, formed in the absence of water, are more stable, but such complexes could not exist in the water-saturated solutions in which uranyl nitrate is much more soluble.

My thanks are due to the director of A.E.R.E. for permission to publish this paper. I am also greatly indebted to Dr. E. Glueckauf, who suggested the work, and to Mr. H. A. C. McKay for much valuable help and advice, and to Mr. J. Sutton for his interest and co-operation.

S 60. *The Formation of Complex Ions in Uranyl Sulphate Solution.\** By T. V. ARDEN.

A STUDY made in this laboratory of the reactions of uranyl sulphate with calcium hydroxide and other alkalis throws light on the nature of the complex ions present in uranyl sulphate solutions. The curves obtained as a result of potentiometric and conductiometric titrations, resemble those obtained by Sutton (this vol., p. S 275), but the first precipitate occurs when 0.75 equiv. of alkali has been added. If the solutions are set aside at this point, the pH readings fall, with an increase in the quality of the precipitate, during two weeks. Inflexions on the curves occur at  $\frac{1}{2}$ ,  $\frac{3}{4}$ , 1,  $1\frac{1}{4}$ , and  $1\frac{3}{4}$  equivs. of calcium hydroxide, indicating the formation of  $\text{UO}_2\text{SO}_4\cdot\text{U}_3\text{O}_8^{++}$ ,  $(\text{UO}_2\cdot\text{OH})_2\text{SO}_4\cdot 2\text{U}_3\text{O}_8\cdot\text{OH}^+$ ,  $\text{UO}_2(\text{OH})_2\cdot\text{U}_3\text{O}_8(\text{OH})_2$ ,  $\text{CaO}\cdot 4\text{UO}_3$ , and  $3\text{CaO}\cdot 8\text{UO}_3$ . The last two compounds, which are different from the corresponding sodium salts, can be explained on the basis of the ions  $\text{U}_3\text{O}_8(\text{OH})_3^-$  and  $\text{U}_3\text{O}_8(\text{OH})_4^{--}$  postulated by Sutton, by assuming a composition corresponding to the structure  $(\text{CaO}\cdot 2\text{UO}_3)(\text{CaO}\cdot 6\text{UO}_3)$  and  $(\text{CaO}\cdot 2\text{UO}_3)(2\text{CaO}\cdot 3\text{UO}_3)$ .—CHEMICAL RESEARCH LABORATORY, TEDDINGTON, MIDDLESEX. [*Read, March 29th, 1949.*]

---