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The Relations of Thorium Nitrate and Certain Organic Solvents.[1] The Coördination Number of Th^{4+}

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At constant water and thorium nitrate activities (saturated aqueous thorium nitrate), the thorium nitrate dissolving in isobutyl alcohol, methyl isobutyl ketone, diethyl ether, ethylene glycol diethyl ether and diethylene glycol diethyl ether is accompanied by 6–7 moles of water, and this ratio is not greatly affected by dilution with inert solvent such as carbon tetrachloride. With the dibutyl ethers of ethylene glycol and diethylene glycol the water–thorium ratio is 5. These are consistent with coördination number 8 for the Th^{4+} cation, nitrate ions being partially displaced from the coördination sphere. With tributyl phosphate and dibutyl butylphosphonate, the thorium appears essentially without accompanying water, and with 2–3 molecules of organic phosphate per thorium. It is demonstrated that the solute is monodisperse, and that there is probably a single bond between the organic component and thorium, which leads to a coördination number less than 8, probably 6.

The types of species present in solutions of 2–1 and 3–1 salts in organic solvents are fairly well recognized now. For a 4–1 salt such as thorium nitrate, fundamental data are lacking. Information available on the heats of solution of thorium nitrate in a variety of organic solvents[2] indicates that the solute–solvent relations are basically similar to those with the 2–1 salts.[3–5]

With uranyl nitrate it is possible to follow the change in water content of the organic phase with increasing uranyl nitrate content, after equilibration against aqueous phase, and to demonstrate that generally four moles of water are transferred with each mole of uranyl nitrate,[6] which leads to the deduction that the main species in solution is $UO_2(NO_3)_2(H_2O)_4$. The distribution coefficients for thorium nitrate are not sufficiently favorable to make this technique directly useful. We have therefore chosen to work at the saturation point alone, using varied additions of an inert diluent to the organic solvent. A correction is made to the water content for the solubility of water in the absence of the salt, and the ratio of water to salt dissolved may then be determined. This paper describes the findings of such an attack.

Experimental

Materials.—The thorium nitrate used was commercial reagent hydrated salt. Composition was checked by ignition to ThO_2 and by water determination with Karl Fischer reagent. Isobutyl alcohol, methyl isobutyl ketone, the ethers, carbon tetrachloride, benzene, *n*-heptane and hexadecane were reagent grade or otherwise highest quality solvents.

Tributyl phosphate, tributyl phosphite and dibutyl butylphosphonate were commercial products (Virginia-Carolina Co.). The percentage of phosphorus, carbon and hydrogen analyses are: tributyl phosphate, P, 11.45; C, 53.4; H, 10.5 (theor., P, 11.63; C, 54.1; H, 10.2); tributyl phosphite, P, 11.6–12.1; C, 56.0; H, 10.9 (theor., P, 12.4; C, 57.6; H, 10.9); dibutyl butylphosphonate, P, 12.0; C, 55.7; H, 10.8 (theor., P, 12.4; C, 57.6; H, 10.9). The phosphorus procedures are difficult on these compounds, but there seems to be no significant proportion of free acids present, and the compounds are essentially as formulated. A trifle of water probably accounts for slightly high hydrogen. Tributyl phosphine oxide was prepared by the procedure of Davies and Jones.[7] We are indebted to S. Sykes and Judith Lloyd for preparations of this compound.

Procedures.—Mixtures of solvent under study and diluent were made up by weight. A portion of the mixture was shaken with excess solid thorium nitrate, in reasonably finely divided form. Where necessary, saturated aqueous thorium nitrate was also added to make certain an aqueous phase was present. Six to seven hours of mechanical shak-

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. R. Ferraro, L. I. Katzin and G. Gibson, *J. Nucl. Inorg. Chem.*, **2**, 118 (1956).

[3] L. I. Katzin, D. M. Simon and J. R. Ferraro, THIS JOURNAL, **74**, 1191 (1952).

[4] L. I. Katzin and J. R. Ferraro, *ibid.*, **74**, 6040 (1952).

[5] L. I. Katzin and J. R. Ferraro, *ibid.*, **75**, 3821 (1953).

[6] L. I. Katzin and J. C. Sullivan, *J. Phys. Colloid Chem.*, **55**, 346 (1951).

[7] W. C. Davies and W. J. Jones, *J. Chem. Soc.*, 33 (1929).

ing of paraffin-sealed glass-stoppered erlenmeyer flasks were generally used. With tributyl phosphite, because of the high heat evolution,[2] the addition of solid nitrate was made to the liquid chilled with ice-water. When experiments were carried out other than at room temperature (2 ± 1° and 45 ± 1°) which was 25 ± 2°, magnetic stirring of the mixture was used.

Following equilibration, the mixtures were allowed to settle, and the organic layer was further centrifuged. Samples 0.2–1.0 g. in weight were taken for water analysis. Thorium analyses on the phosphoörganics were performed gravimetrically by the procedure described below. After this phase of the work was essentially completed, the fluoride indicator titration technique described by Banerjee[8] was adopted and used directly on weighed samples for the alcohol, ketone and ether systems. To avoid liquid phase separation the procedure was modified by addition of 25 ml. of methanol (rather than water[8]) to 10 ml. of buffer solution and 2 ml. of indicator. The procedure was sensitive to about 0.6 mg. of thorium (0.5–1%).

For gravimetric thorium analysis, 1–5 g. samples were added to 30 ml. of CCl_4 in a separatory funnel and extracted with 50 ml. of water. Some 99% of the thorium usually appeared in the water layer, but for certainty this was always followed by further extraction of the organic phase with 30 ml. of a 10% sodium carbonate solution. The pooled aqueous extracts were acidified with 10 ml. of 1:1 HCl and boiled. Thorium was then precipitated with oxalic acid and after suitable digestion the solid was ignited and weighed as ThO_2.

Phosphorus analyses on the solvents depend on reliable decomposition of the compounds. Tributyl phosphate decomposition was achieved by digestion with 55–58% HI.[9] Tributyl phosphite and dibutyl butylphosphonate were decomposed by sodium molybdate-$HClO_4$ oxidation.[9] Magnesium ammonium phosphate was precipitated and ignited to $Mg_2P_2O_7$.

Results

With the reference condition adopted, saturated aqueous thorium nitrate in contact with excess solid, both thorium nitrate and water activities are fixed (the effects of minor amounts of organic material dissolving in the aqueous phase are negligible). Direct comparison of the various equilibrium systems is therefore permissible. Some estimate must be made, however, of "free" water in the organic phase. This is done by equilibrating organic phase against 5 *M* $CaCl_2$, which is isopiestic with saturated thorium nitrate.[10] The water correction made is proportional to the organic content of the equilibrium thorium-bearing organic layer.

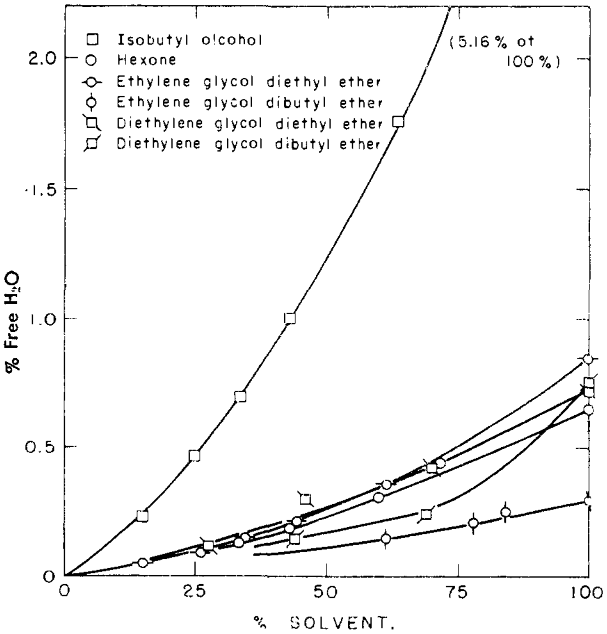

Fig. 1.—Equilibrium water content of solvent–CCl_4 mixtures equilibrated against 5 *M* $CaCl_2$.

The results for a series of experiments with isobutyl alcohol, hexone, diethyl ether and several polyethers are shown in Table I. The corresponding free-water curves are shown in Fig. 1. The thorium nitrate solubility in diisopropyl ether was too low to be of use for the purposes in hand. A value for diethyl ether (20°) exists in the literature,[11] but is apparently too low. Even for isobutyl alcohol and hexone, phase separation was found with the diluent *n*-heptane, so it was not tried with the ethers. With ethylene glycol diethyl ether, and diethylene glycol diethyl ether, phase separation was found even with carbon tetrachloride as diluent.

Table I shows that with isobutyl alcohol, diethyl ether and the diethyl ethers of ethylene glycol and diethylene glycol, 7–7.5 molecules of water are present with each molecule of thorium nitrate in the pure solvent, whereas with methyl isobutyl ketone the figure is about 6.75. Dilution with CCl_4 brings the ratios below 7. With both the isobutyl alcohol and the ketone comparable ratios of 6.2–6.4 are found as the solvent is diluted with carbon tetrachloride. The dibutyl ethers of ethylene glycol and diethylene glycol show a sharp departure from this behavior, the water–thorium nitrate ratios being very close to 5, in both instances.

A real difference between the alcohol and the ketone is seen on comparing the thorium content as a function of dilution (Fig. 2). The solvent power of the ketone falls off very quickly below 50% and below about 25% concentration is essentially completely lost. The alcohol seems to dissolve thorium even out to low concentrations of alcohol.

The results of similar experiments with mixtures of CCl_4 and tributyl phosphate, dibutyl butylphosphonate and tributyl phosphite, respectively, are shown in Table II. Benzene diluent and tributyl phosphate gave essentially the same results as the CCl_4 series, and are not reproduced here. Hydrocarbon diluent (*n*-heptane, hexadecane) gave phase separation in the range 75–20% by weight of tributyl phosphate (see the alcohol and ketone tests above) and the data are also omitted from the table.

The striking contrast between the data for tributyl phosphate and dibutyl butylphosphonate, and the data in Table I, is that the solutions are essentially anhydrous—there is, in general, less than 0.5 water molecule per thorium nitrate. Related to this is the essential constancy of the phosphorus–thorium ratio—2.5 for tributyl phosphate, 2.3 for dibutyl butylphosphonate. Taking these facts together, the conclusion results that there is a

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(8) G. Banerjee, *Z. anal. Chem.*, **146**, 417 (1955).

(9) W. R. Simmons and J. H. Robertson, *Anal. Chem.*, **22**, 294 1950).

(10) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press, Inc., New York, N. Y., 1955.

(11) P. Misciatelli, *Gazz. chim. ital.*, **60**, 833 (1930).

direct, strong reaction between the phosphorus compounds and the thorium nitrate, such that dilution with CCl_4 or other inert diluent does not give much dissociation of the product, and that in the reaction water is stripped from the thorium to give an essentially anhydrous main species in solution. It has been shown by others[12,13] that the action of tributyl phosphate in extracting thorium nitrate from more dilute aqueous solution is relatively little affected by such dilution with inert liquids.

TABLE I

COMPOSITIONS OF ORGANIC LAYERS IN EQUILIBRIUM WITH SATURATED THORIUM NITRATE

Solvent comp. (%)[a]	Th (%)	Th-$(NO_3)_4$ (%)	Water (%)	Water cor. (%)	Excess water (%)	H_2O/Th	Org./Th[b]
Isobutyl alcohol							
100	23.95	49.53	15.75	1.79	13.95	7.5	4.55
71.5	18.68	38.67	11.45	1.22	10.23	7.06	6.0
50.2	13.41	27.76	7.53	0.84	6.69	6.43	7.6
43.0	11.51	23.83	6.18	.70	5.48	6.14	8.2
	10.70	22.13	5.95	.72	5.23	6.30	9.1
33.3	8.22	17.02	4.66	.55	4.11	6.44	10.0
	8.14	16.83	4.42	.55	3.87	6.12	10.1
20.0	3.88	8.03	2.03	.30	1.73	5.75	14.5
9.0	0.78	1.61	0.42	.10	0.32	(5.3)	...
Isobutyl alcohol[c]							
100	23.6	48.8	15.2	2.06	13.1	7.15	
89.8	20.76	42.93	13.42	1.71	11.71	7.27	
77.7	18.40	38.05	11.00	1.37	9.63	6.74	
71.4	16.75	34.64	10.20	1.20	9.00	6.92	
63.8			Phase separation				
Hexone							
100	22.68	46.90	12.15	0.30	11.85	6.74	4.2
	22.23	45.98	11.90	.30	11.60	6.72	4.4
83.5	18.48	38.22	9.46	.28	9.18	6.40	5.5
71.7	15.50	32.06	7.88	.26	7.62	6.33	6.5
60.3	11.69	24.18	6.03	.21	5.82	6.42	8.3
	11.35	23.48	5.66	.21	5.45	6.18	8.7
43.2	4.26	8.81	2.24	.18	2.06	6.23	21
33.5	1.12	2.32	1.27	.12	1.15	13.2	67
25.2	0.21	0.43	0.53	..	...	...	...
20.1	0.00	0.00	0.36	..	...	...	...
Hexone[c]							
92.2	19.20	39.71	9.98	0.70	9.28	6.22	
85.5	17.71	36.63	9.12	.60	8.52	6.20	
78			Phase separation				
Diethyl ether							
100	21.08	43.59	12.38	..[d]	...	7.58	6.5
76.7	14.75	30.50	7.75	..	...	6.78	13
53.7	3.20	6.62	1.66	..	...	6.68	20
36.3	0.54	1.12	0.38	..	...	(4.4)	...
Ethylene glycol diethyl ether							
100	27.90	57.73	16.30	0.22	16.08	7.42	1.8
82.4	24.25	50.15	13.50	.20	13.30	7.07	2.4
			Phase separation				
Ethylene glycol dibutyl ether							
100	14.24	29.46	5.75	0.20	5.55	5.02	6.1
84.1	8.86	18.33	3.69	.19	3.50	5.09	9.9
77.8	6.83	14.13	2.81	.16	2.65	5.00	12.6
61.2	2.50	5.17	1.22	.14	1.08	5.5	31
42.7	0.70	1.45	0.40	.12	0.28	5.1	...
Diethylene glycol diethyl ether							
100	27.80	57.49	16.12	0.19	15.93	7.38	1.36
85.2	25.37	52.47	14.15	.19	13.96	7.09	1.61
			Phase separation				
Diethylene glycol dibutyl ether							
100	21.65	44.79	8.90	0.35	8.55	5.09	2.3
68.9	15.45	31.97	6.42	.10	6.32	5.28	2.9
43.9	8.07	16.70	3.18	.05	3.13	5.00	4.6
26.9	0.96	1.99	0.47	.01	0.46	6.2	29

[a] Per cent. oxygenated component; second component, CCl_4. [b] Oxygenated component/Th, corrected for CCl_4. [c] *n*-Heptane diluent rather than CCl_4. [d] Pure water solubility only 1.25%, so corrections less than for hexone (<0.20 at 100%).

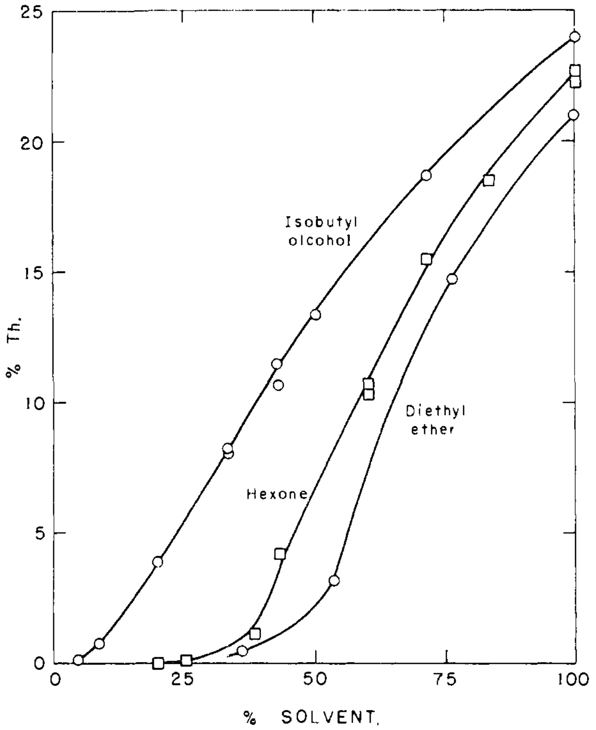

Fig. 2.—Equilibrium thorium content of solvent–CCl_4 mixtures equilibrated against saturated aqueous thorium nitrate plus $Th(NO_3)_4 \cdot 5H_2O$.

The actual values for the phosphorus–thorium ratios—2.50 and about 2.33—suggest the possibility of polymerization. To evaluate this possibility, freezing point depressions in benzene were measured. In one experiment, tributyl phosphate was equilibrated against solid thorium nitrate for three days, and 3.702 g. of the final fluid dissolved in 41.10 g. of benzene. The freezing point depression measured was 0.401°, corresponding to a molecular weight of about 1145. Subsequent thorium analysis of the solution showed 1.96 g. ThO_2 per 100 g. of solution, or a ratio of about 2.4 tributyl phosphates per thorium nitrate in the sample weighed. This ratio corresponds to a molecular weight of about 1115, which may be taken as sufficient agreement with the freezing point data.

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(12) J. C. Warf, THIS JOURNAL, **71**, 3257 (1949).

(13) M. R. Anderson, U. S. Atomic Energy Document ISC-116 (1950).

TABLE II

COMPOSITIONS OF ORGANIC PHOSPHATE LAYERS IN EQUILIBRIUM WITH SATURATED THORIUM NITRATE

Solvent comp. (%)[a]	ThO_2 (%)	$Th(NO_3)_4$ (%)	H_2O (%)	H_2O/Th	P/Th
Tributyl phosphate					
100	22.92	41.67	0.58	0.37	2.50
84.6	20.88	37.96	.49	.34	2.47
59.2	16.24	29.53	.45	.40	2.53
38.4	11.90	21.64	.38	.47	2.50
20.8	6.83	12.41	.15	.32	2.64
6.60	2.18	3.96	.04	.3	2.89
Dibutyl butylphosphonate					
100	24.79	45.07	1.00	0.59	2.30
84.4	22.43	40.78	0.79	.51	2.32
58.2	17.63	32.05	.63	.52	2.35
37.5	12.81	23.29	.38	.44	2.36
20.5	7.84	14.25	.24	.45	2.36
6.28	2.72	4.94	.13	.7	2.33
Tributyl phosphite[b]					
100	27.29	49.61	7.06	3.8	1.68
84.1	25.08	45.59	6.02	3.5	1.72
83.6	24.46	44.47	6.06	3.6	1.79
57.2	19.88	36.14	4.76	3.5	1.80
36.5	14.51	26.38	3.09	3.1	1.87
19.9	7.98	14.51	1.60	2.9	2.22
19.8	8.60	15.63	1.85	3.2	2.00
6.16	2.80	5.09	0.46	2.4	2.20

[a] Second component of solvent, CCl_4. [b] H_2O/Th and P/Th taking water analyses at face value.

TABLE III

EFFECT OF TEMPERATURE ON PHOSPHORUS–THORIUM RATIO AT SATURATION

Solvent	Equil. temp., °C.	Solvent,[b] %	ThO_2, %	Th(NO$_3$), %	H_2O, %	P/Th
Tributyl phosphate	2	53.2	14.75	26.81	0.37	2.61
	45	53.5	15.76	28.65	.53	2.38
Dibutyl butylphosphonate	2	52.7	15.02	27.30	.42	2.67
	45	52.6	17.16	31.20	.50	2.21
Tributyl phosphite	2	52.0	17.57	31.94	3.38	2.01[a]
	45	51.4	18.63	33.87	4.05	1.81[a]

[a] Water analysis at face value; assuming all water fictitious raises ratios 5–6%. [b] Second component, CCl_4.

There is therefore no basis for assuming significant polymerization, and there is confirmation that the amount of free tributyl phosphate is insignificant, or a markedly low molecular weight would be found. The most reasonable explanation is that there is present a mixture of two species, one of which contains two molecules of phosphorus compound per thorium, and one which contains three molecules. With tributyl phosphate at room temperature these two forms are equally abundant, with dibutyl butylphosphonate there is apparently twice as much of the di-phospho form as the tri-phospho. As seen in Table III, the alteration of ratio with temperature is small, but detectable. The water analyses do not completely eliminate the possibility that the form with two molecules of phosphorus compound per thorium nitrate also contains a water molecule, but in all cases there is a small deficiency of water, and it seems unreasonable that there should be no free water whatever in the liquid, when water has a very high solubility in the phosphorus compounds in the absence of thorium nitrate.

The phosphorus compounds contain more than one oxygen atom each, leaving the possibility that they are multiply coördinated to the thorium. Tests were therefore made with tributyl phosphine oxide, containing three C–P bonds, and a single oxygen. A sample of 1.384 g. of tributyl phosphine oxide dissolved in 20.85 g. of benzene was equilibrated with solid thorium nitrate pentahydrate. The freezing point of the final solution was depressed 0.646° under that of pure benzene; for the original tributyl phosphine oxide solution, a depression of 1.55° would have been expected. There was thus found a diminution of the effective solution concentration by a factor of 2.40. Thorium analysis of the solution showed the equivalent of 1.147 g. of thorium nitrate, or a ratio of 2.65 tributyl phosphine oxides per thorium, which might be expected to give a freezing point depression of about 0.59°. Without rationalizing the small difference from the experimental figures, it is clear that the interaction of tributyl phosphine oxide with thorium nitrate is essentially the same as that of tributyl phosphate and that the single oxygen atom bound only to the phosphorus may coördinate strongly enough to account for the experimental findings.

The data for tributyl phosphite (Table II) show apparent water approximating 3.5 molecules per thorium nitrate. There is evidence, however, that some reaction occurs in the presence of thorium nitrate which alters the phosphite,[14] so the compositions found analytically should not be interpreted in the same fashion as for the other compounds.

When tributyl phosphate is diluted with isobutyl alcohol or hexone instead of an inert solvent, there exists the possibility of competition between the two compounds for the thorium. Data on such experiments are given in Table IV. It appears, to a good approximation, that the tributyl phosphate–thorium nitrate interaction is so strong that the total composition of the liquids at equilibrium is closely the sum of the independent systems, tributyl phosphate plus inert diluent, and isobutyl alcohol or hexone plus inert diluent. In making such analysis, concentrations must be compared in mole fraction units, and the assumption made that the inert diluent of the alcohol or ketone system is a compound containing 2.5 formula weights of the tributyl phosphate per mole. The thorium nitrate attributable to the alcohol or ketone is assumed to have the water complement deduced from the data in Table I. Another method of making the comparison is to deduct first the "free" water from the Table I and Fig. 1 data, then assume a hydration for the thorium nitrate, and determine the amount of thorium nitrate excess to the corresponding figure. The ratio of tributyl phosphate to the excess thorium nitrate may then be calculated (see Table III). For the hexone, good constancy at about 2.4 for the ratio is found, with the water–thorium ratio assumed to be 6. With the isobutyl alcohol data, constancy ratios

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[14] L. I. Katzin and R. L. McBeth, unpublished data.

TABLE IV

COMPOSITIONS OF TRIBUTYL PHOSPHATE MIXTURES WITH ISOBUTYL ALCOHOL AND HEXONE SATURATED WITH THORIUM NITRATE

A. Isobutyl alcohol							
Orig. tributyl phosphate, %	78.7	64.7	55.0	44.8	28.8		
$Th(NO_3)_4$, %	42.8	42.5	43.1	43.0	43.4		
H_2O, %	3.00	5.10	6.70	8.32	11.08		
Calcd.[a]							
$Th(NO_3)_4$, %	41.0	42.0	42.6	43.7	45.6		
H_2O, %	3.07	5.39	7.38	9.14	11.4		
Calcd. P/Th[b]							
(a) 6.0 hydration	2.47	2.62	2.81	3.45	...		
(b) 6.8 hydration	2.37	2.39	2.41	2.60	...		
B. Hexone							
Orig. tributyl phosphate, %	85.0	78.4	64.5	54.7	44.8	28.7	19.6
$Th(NO_3)_4$, %	41.0	41.3	40.3	40.9	40.8	42.4	43.3
H_2O, %	1.29	1.87	3.06	4.16	5.27	7.51	8.85
Calcd.[a]							
$Th(NO_3)_4$, %	39.5	39.3	40.2	40.9	41.9	43.6	44.6
H_2O, %	1.27	2.03	4.07	5.39	6.72	8.79	9.82
Calcd. P/Th[b] (6.0 hydration)	2.48	2.39	2.37	2.30	2.35	2.49	3.2

[a] From two solvent–CCl_4 systems, as per text. [b] After deducting "free" water, and deducting $Th(NO_3)_4$ ascribed to remaining water per ratio indicated.

are as for the hexone system, but both are a trifle less (2.4 as against 2.5) than for the phosphate–carbon tetrachloride system. At the lower phosphate concentrations, which might show some shifts, the corrections and approximations become too large to yield any reliable ratios.

Discussion

Thorium nitrate dissolved in isobutyl alcohol, methyl isobutyl ketone, diethyl ether, ethylene glycol diethyl ether or diethylene glycol diethyl ether, under the reference conditions of thorium nitrate activity and water activity, is accompanied by about 7 molecules of water. When the organic phase is somewhat diluted with carbon tetrachloride, the ratio drops toward 6. The concurrence of the data between these different solvents, and the relative insensitivity to dilution with inert solvent, give support to the interpretation that basically the same species is present in the different solvents, with perhaps a little variation in the exact average water content of a solute molecule. The basic hydration number may be taken to be 6, from the effects of CCl_4 dilution on the isobutyl alcohol, ketone and ethyl ether systems.

From measurements of the heat of solution of the thorium nitrate hydrates in these and other solvents it has already been suggested[2] that the coördination number of thorium in these systems might be 8, and that of the four anions accompanying the thorium, one or two might be displaced from the coördination sphere by a solvent molecule. The results of the present experiments indicate this presumption to be reasonable, and that in the saturated system, assuming the coördination number 8, water displaces on the average two of the anions to give the apparent hydration 6. Some partial displacement of another anion may account in part for the small deviations from the exact number, though they may also be ascribable to the assumptions made of constancy of the "free water" values for the solutions.

A different situation is found with the *dibutyl* ethers of ethylene glycol and diethylene glycol. Here the water–thorium ratio is close to 5.0. This could still represent the coördination number 8, but with only one anion displaced by water. Whether another is displaced by an ether oxygen is not certain, but debatable. With the polyether systems, the mole ratio of organic component to thorium drops below 2 for the diethyl ethers of both ethylene glycol and diethylene glycol. It is impossible to say with certainty whether the behavior is due to direct coördination of solvent to cation, or whether the effect of the multiple ether linkages is only to make an environment more compatible with the hydrated thorium nitrate species. However, if it were the former case, one would expect diisopropyl ether to show more salt solubility than it does, and one would not expect the water–thorium relationship to be as independent of solvent as it is.

With dibutyl butylphosphonate and tributyl phosphate it seems clear that one is dealing with a new coördination number for thorium, less than 8. It seems more likely that it is 6 than 7, and that the forms with three phosphate molecules per thorium probably arise from replacement of one of the anions in the coördination sphere, rather than by occupying a third position in addition to four occupied by anions. The status of the small amount of water found in the solutions is obscure, and one would tend to ascribe it to adventitious or "free" water rather than to water occupying a third coördination position in the species containing only two phosphate groups.

Cations which are known to show more than one coördination number are Co(II), Ni(II), Fe(III) and Hg(II), and possibly Ru(II), Os(II), Pt(II) and Pd(II). It seems very probable that with further investigation more examples will be identified, but Th(IV) represents an important addition to the group, as the major tetravalent cation. Tributyl phosphate dissolves uranyl nitrate in essentially anhydrous condition,[14,15] and with two tributyl phosphates per uranyl nitrate, suggesting again coördination number 4, as against the normal 6.[6] Americium nitrate also interacts strongly with tributyl phosphate.[16]

If in this case also a lower coördination number obtains, there is room for speculation that in these three heavy elements the multiplicity of coördination numbers may be linked with the use of d-orbitals, as seems the case with most of the lighter elements enumerated above.

Of importance in these considerations is the relation of the group coördinated to the coördination number of the cation. With Co(II), for example, the lower coördination number is never achieved with nitrate as the anion, but represents the common state in organic solution with the halides. With Fe(III), the lower coördination number is again found with chloride in organic solution. The ability of tributyl phosphate similarly to influence the coördination number of the cation is established at least with Th(IV) and uranyl ions, and may be expected to extend to others also.

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(15) H. A. C. McKay and T. V. Healy, *Rec. trav. chim.*, in press.

(16) K. A. Walsh, Nuclear Engineering and Science Congress, Cleveland, Ohio, December, 1955, paper 270.

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Heat Capacity and Thermodynamic Functions of Uranium(IV) Oxychloride and Uranium (IV) Oxybromide from 10 to 350°K.[1]

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Low temperature heat capacity measurements have been made on uranium(IV) oxychloride and uranium(IV) oxybromide, and the data have been used to calculate the entropy, enthalpy and free energy functions for these substances. At 298.16°K., the molal values of C_p, $S°$ and $H° - H_0°$ are 22.72 ± 0.03 cal./deg., 33.06 ± 0.05 cal./deg., and 4586 ± 7 cal., respectively, for $UOCl_2$, and 23.42 ± 0.03 cal./deg., 37.66 ± 0.06 cal./deg., and 4989 ± 7 cal. for $UOBr_2$.

The present study was undertaken to supplement the available chemical thermodynamic data on the uranium oxyhalides and to investigate by calorimetric measurements the possible occurrence of low temperature magnetic transformations in uranium(IV) oxychloride and uranium(IV) oxybromide. The presence of such phenomena in UO_2[2-4] and UI_3[5] has already been demonstrated.

Experimental

Preparation of Uranium Dioxide.—Ammonium diuranate, $(NH_4)_2U_2O_7$, was precipitated from hot aqueous solution by treating uranyl nitrate with ammonium hydroxide. The precipitate was washed with hot water, filtered on a sintered-glass Büchner funnel, air-dried at 115°, and, after being ground, was ignited at 700° to U_3O_8. Subsequent reduction to uranium dioxide was achieved in a Vycor apparatus, using hydrogen purified over hot copper and dried over anhydrous magnesium perchlorate. Although most of the reduction took place below 800°, the reactor was maintained at 950–1000° for at least one hour. This procedure yielded a finely divided, brown powder containing 87.76 ± 0.08% uranium (theoretical, 88.15%), determined by ignition in air to U_3O_8.

Preparation of Uranium(IV) Oxychloride.—Anhydrous uranous oxychloride ($UOCl_2$) was prepared on the 200-g. scale by dissolving uranium dioxide in excess molten uranium tetrachloride by the reversible reaction $UO_2 + UCl_4 \rightleftarrows 2UOCl_2$. After the product was cooled and ground the excess UCl_4 was removed *in vacuo* at 450°. Under these conditions disproportionation of the uranous oxychloride is said to be negligible.[6] Uranium tetrachloride (about a 10% excess) prepared in the manner previously described,[7] was ground in an agate mortar with uranium dioxide and transferred to a covered porcelain crucible within a Vycor reactor. After evacuation, the reactor was filled with purified dry nitrogen, placed in a furnace preheated to 600°, and maintained at that temperature for about 40 minutes. After cooling, the reactor was unloaded in a dry box, and the fused product ground. The product was then reloaded into the reactor, heated to 600° under a nitrogen atmosphere for 20 minutes, cooled to 450°, and held at this temperature for 20 minutes while the reactor was evacuated to 10^{-6} mm. in order to permit excess UCl_4 to sublime from the crucible. Analyses by ignition in air to U_3O_8 indicated 72.73 and 72.90% uranium (theoretical, 73.26%); gravimetric determination of chlorine as silver chloride yielded 22.17 ± 0.03% (theoretical, 21.82%).

Since the starting materials in this preparation, essentially equimolar quantities of UCl_4 and UO_2, should yield the same over-all analysis as the product, gross analyses for uranium and chlorine are not sufficient in themselves as an indication of the purity of the product. It was necessary to demonstrate that no appreciable quantities of UCl_4 and/or UO_2 remained in the sample.

X-Ray diffraction analysis indicated that the major constituent and only detectable crystalline phase was $UOCl_2$. Attempts to determine any excess UCl_4, by sublimation from a small sample at 460° in high vacuum, resulted in some disproportionation of the $UOCl_2$, and hence permitted only the establishment of an upper limit of 5% for the UCl_4 content.

Determinations of the amount of UO_2 present in the sample were made by washing a weighed sample on a filtering crucible with 2 *N* HCl and weighing the residue. The results indicated only a negligible trace of UO_2 in the sample.

Since the heat capacity curve of uranium dioxide exhibits a λ-type maximum at 28.7°K.[2,4] with an electronic enthalpy contribution of about 25 cal. for the transition, any UO_2 present as an impurity phase would be expected to show up

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(2) W. M. Jones, J. Gordon and E. A. Long, *J. Chem. Phys.*, **20**, 695 (1952).

(3) A. Arrott and J. E. Goldman, *Phys. Rev.*, **99**, 1641 (1955).

(4) D. W. Osborne and E. F. Westrum, Jr., *J. Chem. Phys.*, **21**, 1884 (1953).

(5) L. D. Roberts, D. E. Lavalle and R. A. Erickson, *ibid.*, **22**, 1145 (1954).

(6) Reported in J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, pp. 588–90.

(7) E. Greenberg and E. F. Westrum, Jr., THIS JOURNAL, **78**, 4526 (1956).