403. *The Osmotic and Activity Coefficients of Uranyl Nitrate, Chloride, and Perchlorate at 25°.*

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Isopiestic vapour pressure measurements have been made on solutions of uranyl nitrate, chloride, and perchlorate at 25° from 0·1 m. to 5·5, 3·2, and 5·5 m., respectively, and the osmotic and activity coefficients of these salts calculated. Some support has been found for the hypothesis that addition of UO_3 leads to formation of the $U_2O_5^{++}$ ion rather than the $UO_2(OH)^+$ ion.

Isopiestic vapour-pressure measurements have already been made on uranyl nitrate (Robinson, Wilson, and Ayling, *J. Amer. Chem. Soc.*, 1942, **64**, 1469), but subsequent measurements on the perchlorate (Boaden, Thesis, Univ. New Zealand, 1946; Stokes, private communication) showed a remarkable variation from one preparation to another. In view of the interest attached to the activity coefficients of these salts (Sutton, *J.*, 1949, S 275; Glueckauf, McKay, and Mathieson, *ibid.*, p. S 299), we have investigated this problem again and find that, although the vapour pressures of these salt solutions are very sensitive to any departure from the exact stoicheiometric ratio of uranium to anion, yet reproducible results can be obtained if care is taken to ensure that this ratio is exact.

Experimental.

Uranyl Nitrate.—The preparation used by Robinson, Wilson, and Ayling (*loc. cit.*) gave a water activity $a_w = 0·8464$ at 2m, the most recent values for the reference salt, potassium chloride, being used. We now find that uranyl nitrate is very difficult to recrystallize from water; if crystals are obtained by excessive boiling and concentration of an acid-free solution, the product is low in the NO_3/U ratio, and its solution has a comparatively high pH and water activity; conversely, if crystals are obtained from even a moderately acid solution, the product is contaminated with acid, the NO_3/U ratio is high, and, on redissolution, low values of pH and water activity are obtained. Only by crystallization from a solution containing the merest trace of acid with only moderate concentration by boiling to give a small yield of crystals (or better, by evaporation at room temperature) can a product be obtained with the stoicheiometric NO_3/U ratio. Five such preparations have been made; in each case the pH was measured at 0·2m and the water activity determined at 2m by equilibration against calcium chloride, with the following results :

Preparation.	A.	B.	C.	D.	E.
pH at 0·2 m.	2·22	2·24	2·34	2·35	2·43
a_w at 2 m.	0·8475	0·8476	0·8472	0·8477	0·8475

Preparations A, C, and E were used for vapour-pressure measurements over the complete concentration range and Table I records the molalities of uranyl nitrate and calcium chloride which were isopiestic. Calculation in the usual way gives the osmotic and activity coefficients shown in Table III.

In addition, solutions were made containing an excess of either UO_3 or HNO_3 and a few isopiestic measurements made in the region of 2m, from which values for uranyl nitrate at exactly 2m could be interpolated as given in Table II.

Uranyl Chloride.—A slight excess of uranium trioxide was dissolved in hydrochloric acid, the solution analysed for uranium as U_3O_8 and chlorine as silver chloride, and the requisite amount of hydrochloric acid added to give the exact Cl/U ratio. Isopiestic measurements (Table I) were made, and osmotic and activity coefficients calculated, but results up to only 3m are reported. At higher concentrations, it was found that hydrogen chloride was lost to the reference calcium chloride solutions on evacuation of the desiccator. A few density measurements at 25° were made as follows :

Molality, m	0·5	1·0	2·0	3·0	4·0
d_4^{25}	1·1393	1·2732	1·5184	1·7378	1·9337

Uranyl Perchlorate.—After dissolution of a slight excess of uranium trioxide in perchloric acid, the solution was analysed for uranium as U_3O_8 and for perchlorate ion by addition of hydrogen peroxide and glass-electrode titration to a pH of 4·5 of the liberated acid with alkali. The method was confirmed by a similar titration of the stock uranyl chloride solution. Perchloric acid was then added in the requisite amount. The results of the vapour-pressure measurements are given in Tables I and III.

TABLE I.

Molalities of isopiestic solutions of calcium chloride and uranyl nitrate, chloride, and perchlorate at 25°.

Uranyl nitrate.

$UO_2(NO_3)_2$.	$CaCl_2$.	$UO_2(NO_3)_2$.	$CaCl_2$.	$UO_2(NO_3)_2$.	$CaCl_2$.	$UO_2(NO_3)_2$.	$CaCl_2$.	$UO_2(NO_3)_2$.	$CaCl_2$.
Preparation A.									
0·9736	1·073	1·724	1·869	2·356	2·472	2·664	2·725	3·035	3·014
1·092	1·202	2·008	2·151	2·473	2·575	2·793	2·837	3·153	3·097
1·216	1·335	2·043	2·188	2·574	2·658	2·942	2·946	3·401	3·241
1·371	1·498	2·282	2·408	2·641	2·707	2·946	2·936	3·587	3·263
1·595	1·733								
Preparation C.									
2·245	2·378	3·127	3·071	3·523	3·329	4·481	3·809	5·106	4·067
2·422	2·538	3·191	3·117	3·894	3·534	4·810	3·951	5·319	4·148
2·661	2·734	3·242	3·152	4·306	3·737	4·971	4·021	5·511	4·235
Preparation E.									
0·1010	0·1032	0·4879	0·5245	0·7737	0·8431	1·288	1·408	1·823	1·969
0·1691	0·1755	0·5484	0·5920	1·041	1·145	1·522	1·659	2·297	2·420
0·3034	0·3213								

Uranyl chloride.

UO_2Cl_2.	$CaCl_2$.	UO_2Cl_2.	$CaCl_2$.	UO_2Cl_2.	$CaCl_2$.	UO_2Cl_2.	$CaCl_2$.	UO_2Cl_2.	$CaCl_2$.
0·1047	0·1065	0·4969	0·5251	1·344	1·413	1·797	1·849	2·442	2·414
0·1328	0·1363	0·6512	0·6903	1·465	1·526	2·030	2·054	2·765	2·686
0·2690	0·2796	0·8087	0·8595	1·706	1·759	2·084	2·105	2·818	2·727
0·3598	0·3766	1·037	1·099	1·777	1·825	2·427	2·404	3·174	3·011
0·3864	0·4048	1·288	1·349						

Uranyl perchlorate.

$UO_2(ClO_4)_2$.	$CaCl_2$.	$UO_2(ClO_4)_2$.	$CaCl_2$.	$UO_2(ClO_4)_2$.	$CaCl_2$.	$UO_2(ClO_4)_2$.	$CaCl_2$.	$UO_2(ClO_4)_2$.	$CaCl_2$.
0·1061	0·1141	0·3806	0·4520	1·602	2·200	2·869	4·090	4·601	6·949
0·1549	0·1714	0·5733	0·7109	1·859	2·580	3·289	4·721	4·853	7·480
0·2078	0·2333	0·7627	0·9773	1·992	2·781	3·687	5·327	5·039	7·897
0·2870	0·3324	0·9657	1·268	2·591	3·667	3·907	5·685	5·179	8·225
0·3634	0·4293	1·329	1·798	2·749	3·907	4·242	6·267	5·458	8·930

TABLE II.

			$\Delta p/p°$:					$\Delta p/p°$:	
HNO_3, m.	UO_3, m.	NO_3/U.	obs.	calc.	HNO_3, m.	UO_3, m.	NO_3/U.	obs.	calc.
0·8356	—	2·418	0·1876	0·1949	—	—	2·000	0·1525	—
0·7020	—	2·351	0·1815	0·1884	—	0·1850	1·831	0·1553	0·1550
0·3743	—	2·187	0·1694	0·1717	—	0·2057	1·813	0·1554	0·1552
0·1785	—	2·089	0·1611	0·1616	—	0·4109	1·659	0·1573	0·1575
0·0894	—	2·045	0·1578	0·1565					

DISCUSSION.

The activity coefficient of uranyl perchlorate reaches very high values at high concentrations and is higher than that of any other electrolyte not excepting magnesium perchlorate. The uranyl ion should therefore be heavily hydrated, and it is difficult to believe that uranyl perchlorate undergoes intermediate or complex-ion formation. If a graph is drawn of log γ against the concentration, the curve for uranyl nitrate occupies a position relative to magnesium nitrate comparable with that of uranyl perchlorate relative to magnesium perchlorate. It might be expected that the curve for uranyl chloride would be found somewhat above that for magnesium chloride. In fact it is only slightly above magnesium chloride in dilute solutions, and in concentrated solutions ($m > 1{\cdot}7$) the activity coefficient of uranyl chloride is actually less than that of magnesium chloride, suggesting that uranyl chloride forms complex salts.

We have applied Stokes and Robinson's "hydration" equation (*J. Amer. Chem. Soc.*, 1948, **70**, 1870) and find that, up to 0·8m the activity coefficient of uranyl chloride can be represented by a hydration number $n = 15{\cdot}1$ and an ionic diameter of 5·30 A. Table III shows the concordance between observed and calculated activity coefficients.

It remains now to discuss the variation of the vapour pressures of uranyl nitrate solutions on addition of excess of nitric acid or uranium trioxide. The results given in Table II are plotted in the figure. This plot represents the change in vapour pressure of a solution which is kept constant at 2m-$UO_2(NO_3)_2$ concentration but to which either nitric acid or uranium trioxide is added. The points are experimental. The straight line on the right of the figure represents the values given in the upper part of the last column of Table II calculated on the assumption that on the addition of nitric acid both uranyl nitrate and nitric acid contribute to the vapour-pressure lowering. The observed lowering is nearly but not quite as great as the calculated, but the difference is small and may well be due to increased intermediate-ion formation ($UO_2NO_3^+$) on addition of excess of nitric acid.

TABLE III.

Osmotic and activity coefficients of uranyl nitrate, chloride, and perchlorate at 25°.

	$UO_2(NO_3)_2$.		UO_2Cl_2.			$UO_2(ClO_4)_2$.	
m	ϕ.	γ.	ϕ.	γ.	γ, calc.	ϕ.	γ.
0·1	0·875	0·551	0·870	0·544	0·543	0·921	0·626
0·2	0·899	0·520	0·890	0·510	0·508	0·972	0·634
0·3	0·928	0·518	0·914	0·520	0·500	1·028	0·669
0·4	0·960	0·526	0·942	0·505	0·504	1·089	0·723
0·5	0·996	0·542	0·975	0·517	0·515	1·152	0·790
0·6	1·031	0·563	1·005	0·532	0·532	1·216	0·871
0·7	1·067	0·587	1·034	0·549	0·552	1·284	0·969
0·8	1·105	0·617	1·066	0·571	0·575	1·356	1·087
0·9	1·143	0·651	1·097	0·595	0·605	1·430	1·226
1·0	1·182	0·689	1·128	0·620	0·638	1·507	1·390
1·2	1·258	0·773	1·188	0·678	—	1·661	1·804
1·4	1·330	0·868	1·247	0·744	—	1·823	2·38
1·6	1·398	0·975	1·303	0·816	—	1·990	3·17
1·8	1·466	1·099	1·356	0·894	—	2·165	4·29
2·0	1·532	1·237	1·406	0·978	—	2·354	5·91
2·5	1·673	1·626	1·530	1·228	—	2·818	13·37
3·0	1·764	2·03	1·655	1·551	—	3·284	30·9
3·5	1·807	2·41	—	—	—	3·721	70·4
4·0	1·809	2·68	—	—	—	4·152	160·2
4·5	1·790	2·89	—	—	—	4·561	358
5·0	1·765	3·06	—	—	—	5·907	750
5·5	1·753	3·25	—	—	—	5·220	1510

Of more interest is the line on the left of the figure. Uranium trioxide may dissolve according to the equation :

$$UO_2^{++} + 2NO_3^- + UO_3 \longrightarrow U_2O_5^{++} + 2NO_3^-$$

$(U_2O_5)(NO_3)_2$ should give a vapour-pressure lowering similar to that of $UO_2(NO_3)_2$ but not necessarily identical. On the assumption that the addition of the trioxide to a uranyl nitrate solution produces $(U_2O_5)(NO_3)_2$, we should expect either that the excess of trioxide would not alter the vapour-pressure lowering or else that it would have only a slight effect. The experimental results show that, if $(U_2O_5)(NO_3)_2$ is formed, there is a slight effect. The present results are consistent with $U_2O_5^{++}$ formation. However, there is another possibility :

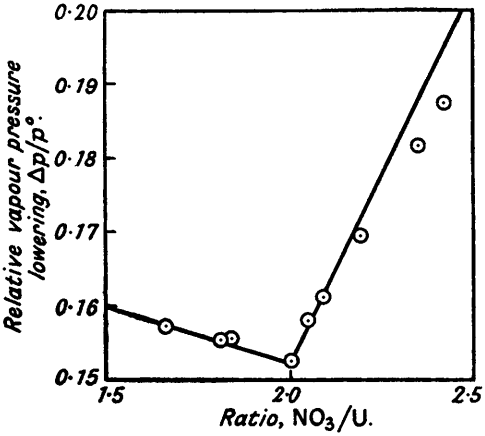
$$UO_2^{++} + 2NO_3^- + UO_3 + H_2O \longrightarrow 2(UO_2{\cdot}OH)^+ + 2NO_3^-$$

The relative vapour-pressure lowering of 2m-$UO_2(NO_3)_2$ is 0·1525. The effect of $UO_2{\cdot}OH^+$ formation is most easily considered by imagining that the process continues to completion, a

2m-$UO_2(NO_3)_2$ solution becoming a 4m-$UO_2(OH)(NO_3)$ solution at $NO_3/U = 1{\cdot}0$. $UO_2{\cdot}OH^+$ must be a large ion, and the relative vapour-pressure lowering of $UO_2(OH)(NO_3)$ should not be very different from that of lithium nitrate which, at a concentration of 4m, is known to be $\Delta p/p^\circ = 0{\cdot}1672$. The complete conversion of 2m-$UO_2(NO_3)_2$ into 4m-$UO_2(OH)(NO_3)$ should lead to a change in $\Delta p/p^\circ$ from 0·1525 to 0·1672, and we cannot be seriously in error if we assume that, should the conversion be incomplete, the change will be *pro rata*. On this assumption, the lower portion of the last column of Table II has been constructed, and the line on the left of the figure drawn. The experimental points lie very close to it, and it follows that we cannot distinguish between $U_2O_5^{++}$ and $UO_2(OH)^+$ formation on grounds of vapour-pressure measurements on the nitrate and, unfortunately, we cannot offer any evidence for or against the hypothesis advanced by Sutton (*loc. cit.*) of $U_2O_5^{++}$ formation.

The perchlorate is, however, different. Our experimental measurements give, at 2m, $\Delta p/p^\circ = 0{\cdot}2216$. If addition of uranium trioxide leads to $U_2O_5(ClO_4)_2$, the vapour-pressure lowering should not be very different. If, however, $UO_2(OH)(ClO_4)$ is formed and the process is complete, a solution of 4m-$UO_2(OH)(ClO_4)$ is obtained whose vapour-pressure lowering should be comparable with that of 4m-lithium perchlorate, which is known to be 0·2056 from Jones's work (*J. Physical Chem.*, 1947, **51**, 516); *i.e.*, addition of the trioxide should, if $UO_2(OH)(ClO_4)$ is formed, *lessen* the vapour-pressure lowering in contrast with the prediction about the hypothetical $UO_2(OH)(NO_3)$. Moreover, if insufficient trioxide is added to effect the complete conversion into $UO_2(OH)(ClO_4)$, the expected vapour-pressure lowering can be calculated without serious error. We therefore made a final experiment, not reported in the experimental section above, of the vapour pressures of three solutions of 2m-$UO_2(ClO_4)_2$ to which uranium trioxide had been added, and compared them with those calculated as described above. We obtained the following results :

Relative vapour-pressure lowering of solutions containing 2m-$UO_2(NO_3)_2$ *and excess of either* UO_3 *or* HNO_3.



The circles are experimental points. The full lines are calculated on the following assumptions : for that on the right, that on the addition of HNO_3 *the vapour-pressure lowerings of* $UO_2(NO_3)_2$ *and* HNO_3 *are additive ; for that on the left, that on addition of excess of* UO_3 *to the solution,* $UO_2(OH)(NO_3)$, *with a vapour-pressure lowering similar to that of* $LiNO_3$, *is formed.*

ClO_4/U	1·685	1·724	1·894	2·000
UO_3, *m*	0·374	0·320	0·112	0
$\Delta p/p^\circ$, obs.	0·2292	0·2290	0·2252	0·2216
$\Delta p/p^\circ$, calc.	0·2167	0·2172	0·2199	(0·2216)

This experiment shows that the addition of uranium trioxide *increases* the vapour-pressure lowering instead of *decreasing* it as is predicted if $UO_2(OH)(ClO_4)$ is formed. Hence, whilst we cannot claim that our experiments prove the formation of $U_2O_5(ClO_4)_2$, they are consistent with this hypothesis, whilst the formation of $UO_2(OH)(ClO_4)$ is not consistent with experiment. To this extent we can support Sutton's hypothesis.

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