324. *Anion Exchange in Uranyl Sulphate Solution. High-concentration Effects and Rate Studies.*

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The concentration of uranium and sulphate in anion-exchange resins in equilibrium with concentrated solutions of uranyl sulphate, UO_2SO_4, is higher than the saturation values for $UO_2(SO_4)_3^{4-}$, $UO_2(SO_4)_2^{2-}$, or $U_2O_5(SO_4)_3^{4-}$. The increase may be due to the presence of $U_2O_5(SO_4)_2^{2-}$, or more probably to the permeation of undissociated UO_2SO_4 into the resin, in addition to the normal exchange process. In dilute solution the rate of adsorption of uranium decreases with increasing pH, owing to the lower rate of diffusion through the resin of $U_2O_5(SO_4)_3^{4-}$ than $UO_2(SO_4)_3^{4-}$.

The adsorption of uranium by strongly basic anion-exchange resins from dilute acid solutions of uranyl sulphate is now well established. It has been demonstrated [1] that in dilute acid solutions (M/200, pH <2) all observations could be explained on the basis of the adsorption under equilibrium conditions of $UO_2(SO_4)_3^{4-}$ and HSO_4^- only. Increases in resin loading at higher pH were shown to be due to the presence of $U_2O_5(SO_4)_3^{4-}$. Other workers [2,3] have claimed that these increases were due to the presence of $UO_2(SO_4)_2^{2-}$, but it was considered by Arden and Wood [1] that this ion would be adsorbed only from relatively concentrated solutions. Hartley [4] observed that when uranium was adsorbed from highly concentrated solutions very high resin loadings were obtained, and the complex adsorbed appeared from analysis to be UO_2SO_4. His tentative explanation of this phenomenon assumed the formation of basic complexes of the type $UO_3SO_4^{2-}$. The same analytical results would be given by a complex $U_2O_5(SO_4)_2^{2-}$, which would complete the series suggested by Arden and Wood. Explanations of the effects of increasing pH and concentration are thus conflicting, although there is general agreement on the results obtained with dilute acid solutions. In an attempt to clarify this situation, we have studied high-concentration effects.

The experimental results already obtained would in some cases be invalidated if equilibria which had been assumed had not been attained. It has already been shown [1,5] that the rate of exchange of the uranium complex for chloride is less than that of sulphate

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[1] Arden and Wood, *J.*, 1956, 1596.
[2] Grinstead, Ellis, and Olson, Paper P/522, Geneva Conference, 1955.
[3] O'Connor, ACCO 61 (U.S. Atomic Energy Commission), 1954.
[4] Hartley, Report GL/CR/CR/9, Dept. of Mines, Australia.
[5] Wood and Benham, Report CRL/AE 123, Chemical Research Laboratory.

TABLE 1.

Solution			Observed uptake (mmoles/g.)		Observed molar ratios				Corrected uptake (mmoles/g.)		Corrected ratios		
$[UO_2^{2+}]$	$[SO_4^{2-}]$	pH	UO_2	SO_4	$\frac{SO_4}{UO_2}$	$\frac{Cl}{UO_2}$	$\frac{Cl}{SO_4}$	P *	UO_2	SO_4	$\frac{SO_4}{UO_2}$	$\frac{Cl}{UO_2}$	$\frac{Cl}{SO_4}$
0·0066	0·0081	3·59	1·095	—	—	3·30	—	—	1·09	—	—	3·36	—
0·0166	0·0203	3·37	1·26	2·82	2·24	2·92	1·30	0·01	1·27	2·81	2·22	2·89	1·31
0·0331	0·0406	3·19	1·38	—	—	2·66	—	0·02	1·36	—	—	2·70	—
0·0663	0·0812	3·00	1·52	3·08	2·03	2·42	1·29	0·04	1·48	3·04	2·05	2·48	1·21
0·133	0·162	2·72	1·73	—	—	2·12	—	0·07	1·66	—	—	2·21	—
0·331	0·406	2·40	2·00	3·49	1·74	1·83	1·05	0·19	1·81	3·30	1·82	2·03	1·11
0·442	0·609	2·20	2·11	—	—	1·73	—	0·26	1·85	—	—	1·98	—
0·663	0·812	2·10	2·28	3·74	1·64	1·59	0·97	0·40	1·88	3·34	1·77	1·96	1·10
0·828	1·015	1·97	2·40	—	—	1·52	—	0·51	1·89	—	—	1·94	—
0·994	1·218	1·89	2·45	3·93	1·60	1·48	0·93	0·61	1·84	3·32	1·81	1·99	1·11
1·160	1·421	1·75	2·57	—	—	1·41	—	0·71	1·86	—	—	1·98	—
1·325	1·624	1·71	2·64	4·14	1·52	1·33	0·88	0·86	1·78	3·28	1·84	2·05	1·12

* Permeation correction, see p. 1712.

TABLE 2. pH 1·86.

Time	Quantity sorbed				Concentration			Charge			
(min.)	UO_2	SO_4	Cl	$\frac{Cl}{SO_4}$	$\{UO_2\}_1$	$\{UO_2\}_2$	$\{SO_4\}_t$	$(UO_2)_1$	$(UO_2)_2$	$(SO_4)_t$	Total
1	0·143	0·907	1·52	1·68	0·143	—	0·478	0·57	—	0·95	1·52
2	0·213	1·23	2·01	1·64	0·213	—	0·59	0·85	—	1·18	2·03
5	0·293	1·83	3·04	1·66	0·293	—	0·95	1·17	—	1·90	3·07
10	0·418	2·20	3·61	1·64	0·418	—	0·95	1·67	—	1·90	3·57
30	0·577	2·42	3·66	1·48	0·577	—	0·69	2·30	—	1·38	3·68
60	0·691	2·53	3·70	1·46	0·691	—	0·45	2·76	—	0·90	3·66
120	0·772	2·63	3·72	1·42	0·772	—	0·31	3·09	—	0·62	3·71
240	0·914	2·76	3·74	1·38	0·914	—	0·02	3·65	—	0·04	3·69
360	0·924	2·74	3·78	1·38	0·924	—	−0·02	3·70	—	—	3·70
480	0·935	2·82	3·80	1·37	0·935	—	0·02	3·74	—	—	3·74
960	0·957	2·88	3·83	1·34	0·957	—	0·01	3·82	—	—	3·82
1440	0·965	2·88	3·86	1·34	0·965	—	−0·01	3·85	—	—	3·85

TABLE 3. pH 3·60.

1	0·153	0·832	1·38	1·66	0·15	0	0·41	0·60	0	0·82	1·42
2	0·200	1·12	1·83	1·63	0·20	0	0·51	0·80	0	1·02	1·82
5	0·341	1·68	2·69	1·60	0·33	0·01	0·68	1·32	0·02	1·36	2·70
10	0·42	2·05	3·23	1·58	0·42	0	0·75	1·68	0	1·50	3·18
30	0·56	2·35	3·67	1·57	0·47	0·09	0·80	1·88	0·18	1·60	3·66
60	0·745	2·49	3·67	1·48	0·55	0·20	0·52	2·20	0·40	1·04	3·64
120	0·910	2·63	3·69	1·40	0·66	0·25	0·24	2·64	0·50	0·48	3·62
240	1·10	2·74	3·75	1·37	0·69	0·41	0·07	2·76	0·82	0·14	3·72
360	1·10	2·80	3·78	1·46	0·71	0·39	0·08	2·84	0·78	0·16	3·78
480	1·11	2·84	3·82	1·35	0·75	0·36	0·04	3·00	0·72	0·08	3·80
960	1·13	2·88	3·84	1·33	0·79	0·34	0	3·16	0·68	0	3·84
1440	1·14	2·91	3·89	1·33	0·79	0·35	0	3·16	0·70	0	3·86

TABLE 4. pH 4·45.

1	0·104	0·669	1·25	1·87	0	0·104	0·57	—	0·21	1·08	1·29
2	0·156	1·03	1·95	1·89	0	0·156	0·86	—	0·31	1·72	2·03
5	0·240	1·58	2·94	1·86	0	0·240	1·25	—	0·48	2·50	2·98
10	0·297	1·82	3·32	1·83	0·02	0·28	1·33	0·08	0·56	2·66	3·30
30	0·454	2·08	3·67	1·76	0·05	0·40	1·34	0·20	0·80	2·68	3·68
60	0·570	2·19	3·68	1·68	0·13	0·44	1·11	0·52	0·88	2·22	3·62
120	0·780	2·35	3·68	1·57	0·24	0·54	0·79	0·96	1·08	1·58	3·62
240	0·981	2·50	3·70	1·48	0·32	0·66	0·55	1·28	1·32	1·10	3·70
360	1·08	2·57	3·72	1·44	0·34	0·74	0·45	1·36	1·48	0·90	3·74
480	1·17	2·61	3·72	1·42	0·33	0·84	0·37	1·32	1·68	0·74	3·74
960	1·32	2·70	3·75	1·38	0·33	0·99	0·21	1·32	1·98	0·41	3·71
1440	1·45	2·80	3·80	1·36	0·35	1·10	0·10	1·40	2·20	0·20	3·80

TABLE 5. pH 4·95.

1	0·082	0·890	1·65	1·96	0·05	0·03	0·69	0·20	0·06	1·38	1·64
2	0·108	1·20	2·20	1·84	0·09	0·02	0·90	0·36	0·04	1·80	2·20
5	0·166	1·58	2·94	1·74	0·05	0·12	1·24	0·20	0·24	2·48	2·92
10	0·222	1·82	3·35	1·84	0·07	0·16	1·38	0·28	0·32	2·76	3·36
30	0·370	2·06	3·64	1·75	0·09	0·28	1·33	0·36	0·56	2·66	3·58
60	0·500	2·14	3·67	1·72	0·11	0·39	1·22	0·44	0·78	2·44	3·66
120	0·686	2·26	3·70	1·62	0·13	0·56	1·03	0·52	1·12	2·06	3·70

or bisulphate. Recent work [6] has shown that the rate of uptake of uranium decreases with increasing pH. These phenomena have now been examined in more detail.

EXPERIMENTAL

The resins used were samples of De-Acidite FF having capacities of 3·67 and 3·85 mequiv./g., and weight swelling * (in the chloride form) of 0·60 g./g. For the saturation tests, a solution of uranyl sulphate was prepared containing 1·325M-uranyl ion and 1·624M-sulphate ion at pH 1·71. This was diluted to various concentrations down to 0·0066M UO_2^{2+}. Samples of approx. 2 g. of moist resin were placed in centrifuge tubes closed with sintered discs, and a large excess of each test solution passed during several hours. The liquor was then centrifuged off, and the adsorbed uranium and sulphate were eluted from the resin with a solution containing 0·9M-sodium chloride and 0·1M-hydrochloric acid and were analysed by standard methods. The resins were finally reconverted into the chloride form before being dried and weighed. A correction for the residual interstitial liquor, amounting to 0·03 ml. of liquor per g. of dry resin chloride, was made by Kraus and Moore's method.[7] The results are given in cols. 1—5 of Table 1.

The water contents of the centrifuged resins after equilibration were measured in separate tests, and found to vary from 0·58 g. per g. of dry resin chloride at 0·33M to 0·56 g. per g. at 1·2M. The specific gravities of the test solutions varied linearly with concentration of uranyl sulphate from 1·00 at zero to 1·414 at 1·21M.

For the rate measurements, two techniques were used according to the total time involved. For periods of 30 min. or more the resin sample, initially in the chloride form, was agitated continuously at 25° with a large excess of test solution, and was then washed with the same solution into a centrifuge tube. As soon as the whole of the resin had been transferred it was drained under vaccum, and then centrifuged. The time was measured from the first contact of resin and solution to the moment of sucking dry. For times of less than 30 min. this procedure was insufficiently accurate, and the centrifuge tube was used as a filter throughout. The test solution was passed at a rate of 260 ml./min., giving a residence time of only 0·23 sec. At this high rate, the concentration of the liquor was not significantly altered by its passage through the resin, and it has been assumed that the resin was in contact with a solution of constant composition. The times were measured from the first application of liquor to the moment of sucking dry; and the resin was then centrifuged as above before elution and analysis.

The solutions used contained 0·0106M-uranyl ion and 0·0322M-sulphate, the pH values being adjusted to 1·86, 3·60, 4·45, and 4·95 by means of sodium hydroxide in four separate tests. The solution at pH 4·95 was metastable, and it was found impossible to continue the test for more than 2 hr. In the other three cases measurements were made up to 24 hr.

Columns 2—4 of Tables 2—5 give the quantities of uranyl and sulphate ion adsorbed, and chloride desorbed (each as mmoles per g. of dry resin chloride) after various periods. The significance of the remaining columns is discussed below.

DISCUSSION

Adsorption from Concentrated Solution.—The results in Table 1 show that resin loadings increase rapidly with increasing concentration of uranyl sulphate in solution. When this exceeds 0·133M the loading is above the saturation value for $UO_2(SO_4)_2^{2-}$ or $U_2O_5(SO_4)_3^{4-}$, the highest figure recorded being almost double this value. This observation, which is in agreement with Hartley's, could result from the adsorption of $U_2O_5(SO_4)_2^{2-}$, and it is clear that mixtures on the resin of this ion with $UO_2(SO_4)_2^{2-}$ could give results agreeing approximately with the observed figures.

From mass-action considerations, high solution concentrations would be expected to favour the adsorption of these bivalent complexes, in competition with the quadrivalent ions. Nevertheless, the experimental results diverge sufficiently from the theoretical figures [$U_2O_5(SO_4)_2^{2-}$ requires molar ratios SO_4/UO_2 1·0, Cl/UO_2 1·0, Cl/SO_4 1·0; $UO_2(SO_4)_2^{2-}$ requires SO_4/UO_2 2·0, Cl/UO_2 2·0, Cl/SO_4 1·0] to suggest that this postulation can at best be only partly correct.

* Measured by Pepper's technique (*J. Appl. Chem.*, 1951, 124).

[6] Napier, personal communication.

[7] Kraus and Moore, *J. Amer. Chem. Soc.*, 1953, **75**, 1497.

The measured uptakes of uranium and sulphate include the quantities due to the permeation of undissociated UO_2SO_4 into the resin beads. It was shown by Betts and Michels[8] that uranyl sulphate is strongly associated in acid solution. Although our tests differ from theirs in that higher concentrations of uranyl sulphate have been used, with less free acid, it is considered that their conclusions would apply to an equal or greater extent to the most concentrated solutions of Table 1. The water content and specific gravities were used to calculate the quantity of uranyl sulphate which would be present inside the resin beads, on the assumption that the concentration in the water in the gel is identical with that in the surrounding solution. The results of this calculation are given in column 9 of Table 1 (*P*). The basis of calculation becomes less justifiable with decreasing concentration in solution, and the corrections in col. 9 become correspondingly too large. As, however, the figures themselves decrease rapidly with concentration, the errors in them will not be large.

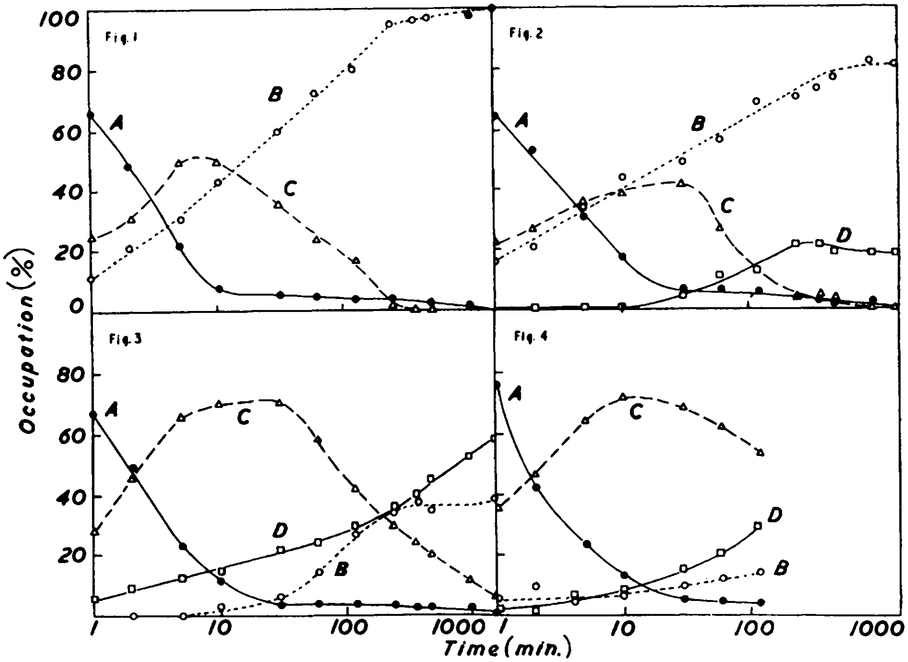

FIG. 1, pH 1·86; FIG. 2, pH 3·6; FIG. 3, pH, 4·45; FIG. 4, pH 4·95.
A, Cl^-; *B*, $UO_2(SO_4)_3^{4-}$; *C*, SO_4^{2-}; *D*, $U_2O_5(SO_4)_3^{4-}$.

The corrected ratios SO_4/UO_2 and Cl/UO_2 rise, and the ratio Cl/SO_4 falls, with increasing concentration up to 0·33M, after which constant values of 1·8, 2·0, and 1·1 respectively are maintained up to the highest concentration which could be achieved without crystallisation. These constant values suggest the presence of one ion only, since values for a mixture of ions would normally change with varying solution conditions.

The calculated values are not in exact agreement with those required for any ion which has been postulated, and it is clear that the factors governing equilibrium in highly concentrated solutions are not completely understood. The ion which most closely corresponds with the calculated ratios is $UO_2(SO_4)_2^{2-}$, and it is considered that the enhanced resin loadings observed by Hartley and ourselves in concentrated solution can best be explained by postulating the permeation of UO_2SO_4 into resin already saturated with $UO_2(SO_4)_2^{2-}$

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[8] Betts and Michels, *J.*, 1949, S 286.

The variations of uranium adsorption can thus be explained as follows. In dilute acid solution (M/200, pH <2), the only ions adsorbed to a measurable extent are $UO_2(SO_4)_3^{4-}$ and HSO_4^-, the adsorption of the latter decreasing to zero as the pH rises to 2·0. Increase in pH at the same concentration causes adsorption of $U_2O_5(SO_4)_3^{4-}$. Increase in concentration at low pH favours the adsorption of $UO_2(SO_4)_2^{2-}$, which displaces all other ions at concentrations greater than 0·3M in solution. It is to be expected that a combination of high pH and high concentration would favour adsorption of $U_2O_5(SO_4)_2^{2-}$, but these conditions cannot be achieved experimentally.

Rate Tests.—Comparison of the uranium uptake figures in Tables 2—5 shows that the initial rate of sorption is greatest below pH 4·0 and decreases with increasing pH in agreement with Napier's observations. The value Cl/SO_4 tends in each case to a final figure of 1·33, suggesting that at equilibrium a mixture of $UO_2(SO_4)_3^{4-}$ and $U_2O_5(SO_4)_3^{4-}$ is present on the resin. If, following Arden and Wood's reasoning, it is assumed that before equilibrium is reached these two ions are present, together with free SO_4^{2-}, the concentration of each ion may be calculated as follows: Let $\{UO_2\}_m$ and $\{SO_4\}_m$ represent the measured quantities sorbed, and $\{Cl\}_m$ the measured quantity desorbed, each as mmoles per g. of dry resin chloride, and let $\{SO_4\}_f$, $\{UO_2\}_1$, and $\{UO_2\}_2$ represent respectively the quantities of free sulphate and of uranium sorbed as $UO_2(SO_4)_3^{4-}$ and $U_2O_5(SO_4)_3^{4-}$ (as mmoles of UO_2 per g. of dry resin chloride).

Then

$$\begin{aligned} \{UO_2\}_1 + \{UO_2\}_2 &= \{UO_2\}_m \\ 3\{UO_2\}_1 + 1{\cdot}5\{UO_2\}_2 + \{SO_4\}_f &= \{SO_4\}_m \\ 4\{UO_2\}_1 + 2\{UO_2\}_2 + 2\{SO_4\}_f &= \{Cl\}_m \end{aligned}$$

Whence

$$\begin{aligned} \{UO_2\}_1 &= 2\{SO_4\}_m - \{Cl\}_m - \{UO_2\}_m \\ \{UO_2\}_2 &= 2\{UO_2\}_m - 2\{SO_4\}_m + \{Cl\}_m \\ \{SO_4\}_f &= 1{\cdot}5\{Cl\}_m - 2\{SO_4\}_m \end{aligned}$$

The calculated values for $\{UO_2\}_1$, $\{UO_2\}_2$, and $\{SO_4\}_f$ are given in Tables 2—5, together with the total negative charges associated with each of these ions. From these results the percentage of active groups occupied by each of these ions and by chloride have been calculated, the results being plotted in Figs. 1—4. These results show that, initially, uranium complexes and sulphate are simultaneously adsorbed by the resin in exchange for chloride, after which the free sulphate gradually disappears, being replaced by complex.

The rate of adsorption of the higher complex is considerably slower than that of $UO_2(SO_4)_3^{4-}$, whose adsorption is substantially complete in all tests after about 300 minutes. At pH 3·6, when the proportion of $U_2O_5(SO_4)_3^{4-}$ adsorbed is small, its maximum concentration is reached in approximately the same time, but at pH 4·45, when the greater proportion of the active groups become occupied by the higher complex, its concentration is still rising steadily after 24 hours, the replacement of free sulphate being correspondingly incomplete. At pH 4·95 the rate of fall of free sulphate is still lower in the region tested. It follows that the rate of adsorption of $U_2O_5(SO_4)_3^{4-}$ decreases as its final concentration increases, suggesting that the adsorption of the larger anion in the outer layers of the resin particles causes steric interference with the further penetration into the interior of the resin molecule. It is not possible to interpret the rate data quantitatively, since the method of calculation of Tables 2—5 considerably exaggerates minor analytical errors. It must be considered that Figs. 1—4 give only approximate representations of the mechanism of the adsorption process. Quantitative elucidation will require a technique, such as absorption spectrography in the solid phase, which permits direct measurements of the concentration of each ion in the resin.

We thank the Directors of the Permutit Company Ltd. for permission to publish this paper.

THE PERMUTIT COMPANY LTD., LONDON, W.4.

[*Received, September 26th,* 1956.]