148. *Some Aspects of the Anion-exchange Behaviour of Uranyl Nitrate in the Presence of Other Inorganic Nitrates.*

By J. K. Foreman, I. R. McGowan, and T. D. Smith.

The addition of inorganic nitrates to aqueous solutions of uranyl nitrate enhances the uptake of uranium on the anion-exchange resin Deacidite FF in the order aluminium > calcium > lithium > ammonium. The predominating cause is considered to be the facilitation of formation of nitrate complexes by the uranyl ion, and of the subsequent ion-exchange, due to the decrease in the effective water content of the system resulting from hydration of the added cation. Visible absorption spectra revealed no new peaks ascribable to an anionic uranyl nitrate complex.

Kraus and his co-workers[1] have shown that the anion-exchange behaviour of certain metal ions in hydrochloric acid is markedly influenced by the presence of inorganic chlorides. Similarly the profound effect of aluminium nitrate on the uptake of uranyl uranium on the anion-exchange resin Deacidite FF from aqueous solutions of uranyl nitrate has recently been noted.[2] This study has now been extended to calcium, lithium, and ammonium nitrate, and attempts have been made to correlate the results with changes in visible absorption spectra which occur on the addition of other nitrates to solutions of uranyl nitrate.

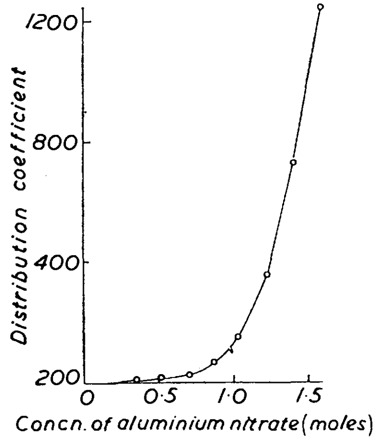

Fig. 1. *Variation of distribution coefficient of uranium with aluminium nitrate concentration.*

Fig. 1 illustrates the size of the increase in the distribution coefficient K_d of uranium (ratio of the equilibrium concentration of uranium in the resin phase to that in the aqueous

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[1] Nelson and Kraus, *J. Amer. Chem. Soc.*, 1954, **76**, 5916; Kraus, Nelson, Clough, and Carlston, *ibid.*, 1955, **77**, 1391; Kraus, Moore, and Nelson, *ibid.*, 1956, **78**, 2692.

[2] Ockenden and Foreman, *Analyst*, 1957, **82**, 592.

phase) on Deacidite FF when increasing amounts of aluminium nitrate are added to aqueous uranyl nitrate. Fig. 2 compares the extents to which aluminium, calcium, lithium, and ammonium nitrates influence the exchange at constant nitrate-ion concentration (6M) maintained by nitric acid. The addition of hydrogen ion, as perchloric or nitric acid, to a fixed concentration of uranyl and aluminium nitrates decreases the uranium uptake (Figs. 3 and 4, curve 1), and addition of ammonium ion (Fig. 4, curve 2) has little influence (cf. Fig. 2).

FIG. 2. *Variation of distribution coefficient of uranium with concentration of* Al, Ca, Li, *and* NH_4 *ions. Nitrate-ion concentration constant at* 6M.

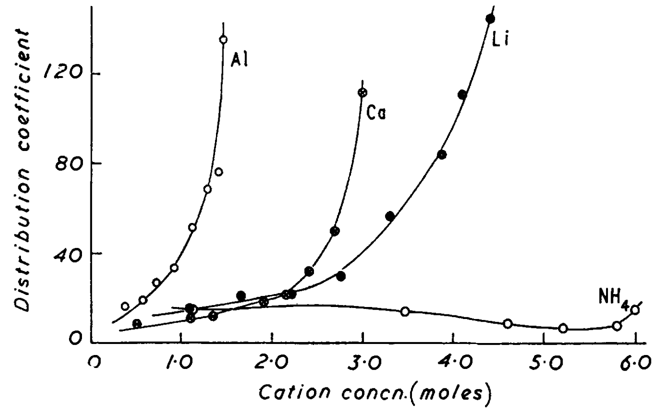


FIG. 3. *Variation of distribution coefficient of uranium with perchloric acid concentration. Aluminium nitrate concentration constant at* 1·3M.

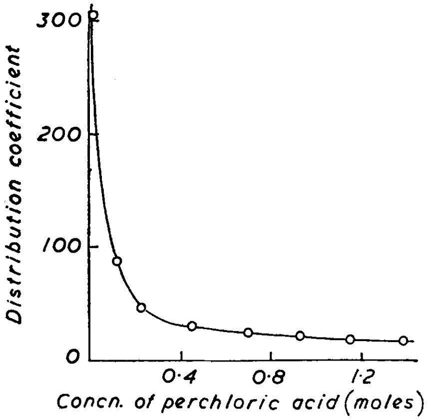
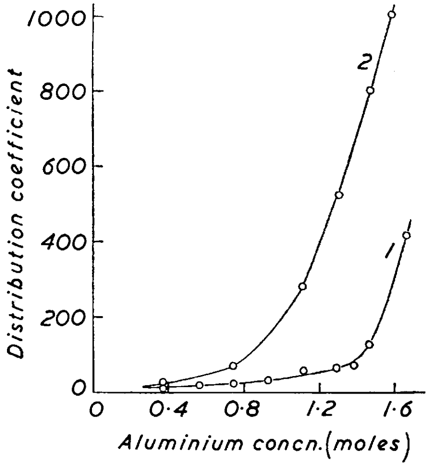


FIG. 4. *Variation of distribution coefficient of uranium with aluminium-ion concentration. Nitrate-ion concentration kept at* 6M *by addition of* (1) *nitric acid and* (2) *ammonium nitrate.*



The greatly enhanced anion-exchange of uranium caused by aluminium, calcium, or lithium nitrate in weakly acid solutions must be attributed to the formation of an anionic nitrate complex of uranium. Formulation of this complex as $UO_2(NO_3)_3^-$, rather than a species of higher negative charge, is supported by the work of Betts and Michels[3] who found that nitrate complex-formation of the uranyl ion is comparatively weak $\{K = [UO_2(NO_3)^+]/[UO_2^{2+}][NO_3^-] = 0{\cdot}21 \pm 0{\cdot}01$ at 5·38M-ionic strength$\}$. Further, from

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[3] Betts and Michels, *J.*, 1949, 286.

spectrophotometric data they found no conclusive evidence for the existence of a higher nitrate complex in nitric acid–sodium nitrate mixtures of ionic strength up to 7·05M. The observed decrease in extent of exchange on addition of nitric acid (Fig. 4, curve 1) may then be reasonably explained as due to formation of the uncharged, associated species $HUO_2(NO_3)_3$ in equilibrium with $UO_2(NO_3)_2$ and nitric acid.

The extent to which uranium is taken up on the resin will depend on the extent of formation of $UO_2(NO_3)_3^-$ and the exchange mechanism by which it is adsorbed. Both these processes will be governed to an appreciable extent by the free water content of the system. In the presence of a high concentration of aluminium nitrate much of this water will be preferentially bound to the aluminium ions, and the formation of the complex uranyl nitrate anion, which involves replacement of water from the hydration sphere of the uranyl ion will be enhanced. Similarly the anion-exchange reaction, which proceeds through removal of water from the hydrated anionic species, will also be facilitated. Since the progressive addition of aluminium nitrate enhances both these effects simultaneously the shape of the distribution coefficient curve can be understood. The smaller abilities of calcium, lithium, and ammonium nitrate to promote anion-exchange of uranium should therefore follow the order of tendency of these cations to be hydrated. If partial molal entropies are taken as a measure of this tendency the values are[4] —74·9, —13·2, 3·4, and 26·9 cal. deg.$^{-1}$ mole^{-1} for the ions Al^{3+}, Ca^{2+}, Li^+, and NH_4^+, the order being that expected. Indeed, the ammonium ion, the least effective in promoting formation of the anionic uranyl nitrate complex, is known to distort the water structure the least of the cations studied, and produces the smallest change in the entropy of water.[5] Hindman[6] has advanced a similar explanation to correlate the relative effectiveness of mixtures of ammonium nitrate and nitric acid, calcium nitrate and nitric acid, and nitric acid alone, in promoting complex-ion formation.

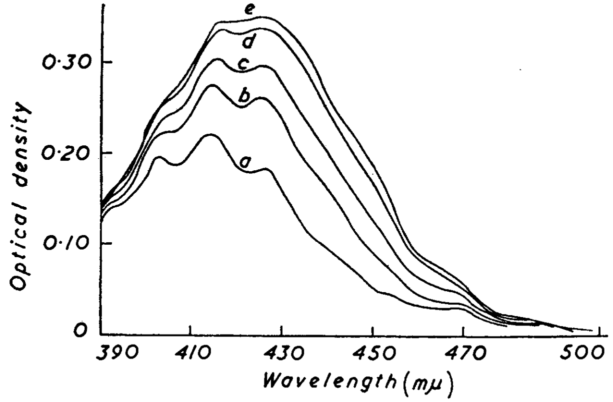

FIG. 5. *Absorption spectra of* 0·005M-*uranyl nitrate*: (*a*) *in water*; (*b*) *in* 0·7M-, (*c*) *in* 1·02M-, (*d*) *in* 1·39M-, *and* (*e*) *in* 1·57M -*aluminium nitrate.*

A second factor increasing the anion-exchange of the uranyl nitrate complex is the variation in activity coefficients of the species present, both in solution and in the resin phase. Such variations are likely to be considerable in the concentrated salt solutions used, but the lack of quantitative data, particularly for resin-phase activities, precludes detailed discussion.

Measurements of the absorption spectrum of uranyl nitrate in the presence of varying quantities of aluminium nitrate indicate that no significant change accompanies the marked increase in distribution coefficient in the region of M-aluminium nitrate, which therefore

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[4] Latimer, " Oxidation Potentials," Prentice Hall, New York, 1952.

[5] Frank and Robinson, *J. Chem. Phys.*, 1940, **8**, 933; Fajans and Johnson, *J. Amer. Chem. Soc.*, 1942, **64**, 668.

[6] Hindman, Paper 45 in "The Transuranium Elements" (Ed. Seaborg, Katz, and Manning), McGraw-Hill, New York, 1949.

cannot readily be associated with higher anionic nitrate complexes, and supports the view that only one anionic complex is formed by the dehydration effect postulated above. Fig. 5 shows that increasing the concentration of aluminium nitrate intensifies the spectral absorption uniformly over the wavelength range 400—470 mμ and no new absorption peaks are revealed. This contrasts with the well-known effect on the spectrum of uranyl nitrate on adding increasing amounts of nitric acid (Fig. 6) where additional absorption peaks occur at 436, 451, and 467 mμ, the intensities of which increase with increasing nitric acid concentration.

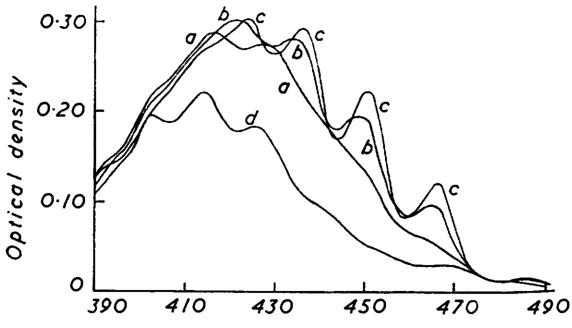

FIG. 6. *Absorption spectra of* 0·005M-*uranyl-nitrate*: (*a*) *in* 4·05M-, (*b*) *in* 9·30M-, *and* (*c*) *in* 13·90M-*nitric acid*; (*d*) *in water*.

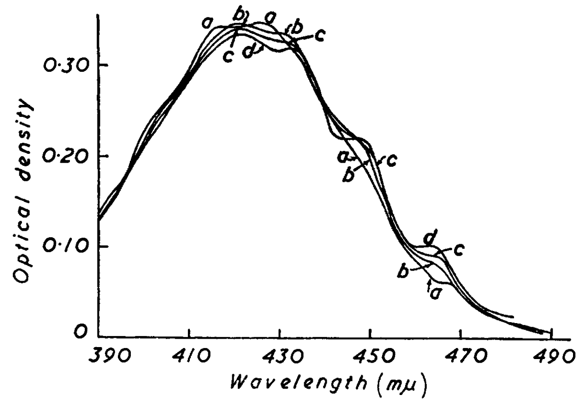

FIG. 7. *Absorption spectra of* 0·005M-*uranyl nitrate in* 1·22M-*aluminium nitrate and constant nitrate concentration of* 6·76M *maintained by ammonium nitrate.* [HNO_3] = (*a*) 0, (*b*) 1·5M, (*c*) 2·33M, (*d*) 3·1M.

Since solutions of uranyl nitrate in nitric acid show very little anion-exchange (see Table), it may be supposed, in agreement with Kaplan *et al.*,[7] that curve *C* of Fig. 6 is due to the presence of an appreciable concentration of the associated species $HUO_2(NO_3)_3$. From their studies on the absorption spectrum of uranyl nitrate in organic solvents in the presence of quaternary ammonium nitrates, where the new peaks noted above are still further intensified, Kaplan *et al.*[7] consider that the singly charged anion $UO_2(NO_3)_3^-$ also exhibits a spectrum of the type shown in Fig. 6, curve *C*. This is apparently at variance with the present work, as Fig. 7 shows. The decreasing anion-exchange observed on the addition of increasing amounts of nitric acid to a solution of uranyl nitrate in aluminium nitrate is paralleled by the increasing growth of the (initially absent) peaks at 436, 451, and 467 mμ, supporting the assignment of the spectrum of Fig. 6, curve *C*, to

Anion-exchange distribution coefficients for uranyl nitrate in nitric acid.

Resin: Deacidite FF. Vol. of solution/weight of resin = 100 : 1.

Acidity (M)	5	6	7	8	9	10
K_d	1	4	11	15	8	3

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[7] Kaplan, Hildebrandt, and Ader, U.S.A.E.C. Report ANL 4520.

$HUO_2(NO_3)_3$. However, no firm conclusion can be drawn from this discrepancy since the present spectra refer to aqueous solutions whereas those of Kaplan *et al.* were derived from solutions in organic solvents and some variation in spectrum from solvent to solvent was observed.

Lower nitrate complexes such as $UO_2(NO_3)^+$ and $UO_2(NO_3)_2$ also contribute to the spectra shown in Figs. 5, 6, and 7. Thus an appreciable spread in values resulted in attempting to calculate the formation constant for $HUO_2(NO_3)_3$ according to $UO_2(NO_3)_3^- + H^+ \rightleftharpoons HUO_2(NO_3)_3$ by the method of Betts and Michels[5] using the data of Fig. 7 (constant $[NO_3^-]$, varying $[H^+]$) at uranium concentrations of 5×10^{-3}M and 1×10^{-2}M, and assuming curve *C*, Fig. 6, to represent the spectrum of $HUO_2(NO_3)_3$. Also optical densities of identical nitrate mixtures but varying uranium concentration do not obey Beer's law. The presence of lower nitrate complexes is consistent with the low values observed[3,8] for the stepwise formation constants of nitrate complexes of the uranyl ion. The spectrophotometric evidence shows that even in strong solutions of aluminium nitrate the formation of $UO_2(NO_3)_3^-$ is far from complete, and the rapid increase in anion-exchange uptake of uranium in aluminium nitrate concentrations of greater than M must be attributed primarily to the facilitation of anion-exchange resulting from hydration of the added aluminium ion as discussed above.

EXPERIMENTAL

Values of distribution coefficients were obtained from batch equilibration experiments in which solutions of the required concentrations were made up, having a constant total volume of 20 ml. and containing constant total amounts of uranyl nitrate (1·040 mg. of U per ml.) and resin (0·200 g.). The mixtures were allowed to equilibrate for 3 days with alternate standing and mechanical shaking. Commercial Deacidite FF was dried at 40°, then ground mechanically, and the particles of 60—85 mesh retained and washed with 3N-sodium hydroxide and then distilled water, the fines being removed by this process. It was converted into the nitrate form by contact with 2N-nitric acid. After filtration and washing with a little water, the resin was allowed to dry in air.

The thiocyanate spectrophotometric method[9] was used to determine the uranium content of solutions, and the absorbancy of the solutions was measured in 2 cm. cells by a Hilger Spekker spectrophotometer with Ilford H.556 filters.

Spectral data were obtained by using a Hilger Uvispek spectrophotometer at 390—500 mμ at 2 or 3 mμ intervals, 4 cm. glass cells being used throughout. The constant uranyl nitrate concentrations employed for this work were 0·005M and 0·010M.

The standard uranyl nitrate solution for anion-exchange studies was prepared by dissolving the requisite amount of pure uranyl nitrate in water. A spectroscopically pure specimen was employed for the spectral investigations. Aluminium nitrate solution was prepared from reagent-grade material, and aluminium analysed as the oxinate. Data for calcium and lithium nitrate solutions were obtained from solubility tables,[10] and perchloric acid by titration with standard alkali. Constancy of total nitrate concentration was achieved by ammonium nitrate addition except where otherwise stated.

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CHEMICAL SERVICES DEPARTMENT, U.K.A.E.A.(I.G.), WINDSCALE WORKS,
SEASCALE, CUMBERLAND.
CHEMISTRY DEPARTMENT, ROYAL COLLEGE OF SCIENCE AND TECHNOLOGY,
GLASGOW, C.1.

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[8] Ahrland, *Acta Chem. Scand.*, 1951, **5**, 1271.

[9] Currah and Beamish, *Analyt. Chem.*, 1947, **19**, 609.

[10] Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Van Nostrand, New York, 1940.