853. *The Spectra and Stability of Some Neptunium Complex Ions in Water and Methanol.*

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The formation constants for $NpO_2^+Cl^-$ and $NpO_2^+NO_3^-$ are found by cation-exchange to be 0.51 ± 0.06 and 0.56 ± 0.06 mole^{-1} l., respectively, in aqueous perchlorate solution of ionic strength 2.0 at $25°$. Absence of complex formation thus cannot be the reason why these anions do not affect the spectrum of Np^V in aqueous solution. Even in methanol, chloride causes no detectable charge-transfer or ligand-field effects in the range 225—1000 mμ, though the 980 mμ peak is shifted to 978 mμ by the change of solvent.

From its relationship to known anion–cation exchange-transfer bands, the ultraviolet absorption of Np^{IV} in aqueous perchlorate solution is assigned to solvent–cation charge-transfer, and this is confirmed by the fact that change of solvent from water to methanol shifts the band in accordance with the difference in solvent ionisation potential. The effect of sulphate on the charge-transfer and ligand-field bands, in water and in methanol, suggests that solvent molecules in the inner sphere are involved. Similar spectra of Fe^{III} and Eu^{III} in water and methanol are noted. Neptunium(VI) does not interact strongly with nitrate ion in water, but the anion–cation charge-transfer band of this system is clearly observed in methanol.

Measurements of the effect of simple anions on the ultraviolet and visible absorption spectra of aqueous solutions of neptunium-(IV) and -(VI) ions have given information about the structure of such systems.[1] Charge-transfer spectra have been used to estimate the overall extent of ionic association, while changes in the ligand-field bands have been interpreted in terms of the number of water molecules between anion and cation. Neptunium(V) ions showed no spectral changes in the range 230—1000 mμ with chloride, nitrate, or sulphate ions in aqueous solution,[2,3] but, in the absence of information about the stability constants, it was not known whether this insensitivity was due to lack of complex formation. Ion-exchange experiments designed to settle this question are now reported, together with a preliminary survey of the behaviour of neptunium ions in methanol. Information of two types should be provided by the change of solvent. Since methanol is less strongly solvating than water, it should be more easily displaced from the cation's solvation shell and so emphasise effects which depend on cation–anion proximity. The fact that the ionisation potential[4] of methanol (10.85 ev) is lower than that of water (12.60 ev) means that bands due to charge-transfer from solvent to cation should be shifted to correspondingly longer wavelengths, and thus be distinguished from bands due to internal transitions of the cation.

Results and Discussion

Np^V *in Water.*—Although Np^V complexes with organic ligands such as oxalate[5] and ethylenediaminetetra-acetate[6] are well known, only qualitative evidence from cation-[7] and anion-[8] exchange experiments appears to be available for interaction with simple anions such as chloride. The uptake of neptunium by the cation-exchange resin Dowex 50WX8 was measured at $25°$ as a function of chloride and nitrate ion concentrations in perchlorate solutions of constant ionic strength (2.0) and hydrogen ion concentration

[1] Sykes and Taylor, *Proc. 7 ICCC*, Stockholm, 1962, p. 31.
[2] Hindman, Magnusson, and LaChapelle, *The Transuranium Elements, Natl. Nuclear Energy Ser. Div. IV*, **14B**, 1949, paper 15.2.
[3] Taylor, Ph.D. thesis (London), 1959.
[4] Watanabe, *J. Chem. Phys.*, 1957, **26**, 542.
[5] Gruen and Katz, *J. Amer. Chem. Soc.*, 1953, **75**, 3772.
[6] Zolotov and Alimarin, *J. Inorg. Nuc. Chem.*, 1963, **25**, 691.
[7] Diamond, Street, and Seaborg, *J. Amer. Chem. Soc.*, 1954, **76**, 1461.
[8] Hyde, *Proc. Internat. Conf. on the Peaceful Uses of Atomic Energy*, Geneva, 1955, **7**, 278.

(2·0M). Table 1 gives the values obtained in duplicate experiments for the distribution coefficient, K_d, defined by

$$K_d = \frac{V}{m}\left(\frac{a_0}{a} - \delta\right) \qquad (1)$$

where V is the volume of the solution, m the mass of resin, a_0 and a the initial and equilibrium concentrations of neptunium in the solution respectively, and δ the swelling factor (0·994). The distribution coefficient, which in perchlorate solution (K°_d) is equal to $16\cdot3 \times 10^{-3}$ l. g.$^{-1}$, decreases reproducibly with ligand concentration as expected for association. If the effect is attributed to the formation of the species $NpO_2^+X^-$ which is not absorbed by the resin, the change in distribution coefficient should follow the equation

$$\frac{K^\circ_d}{K_d} = 1 + Kc \qquad (2)$$

where K is the association constant and c the ligand concentration. The last column of Table 1 gives the values found for K and its standard deviation from the least-squares straight line passing through the origin on the plot of $[(K^\circ_d/K_d) - 1]$ against c. That this treatment adequately represents the data is shown by the calculated values of the distribution coefficient obtained from the association constant. Average values for the

TABLE 1.

Observed and calculated values of the distribution coefficient $10^3 K_d$ (l. g.$^{-1}$) for the adsorption of NpO_2^+ by Dowex 50WX8 from nitrate and chloride solutions.

[X] (M)		0·2	0·4	0·6	0·8	1·0	1·2	1·4	1·6	1·8	K (M^{-1})
NO_3^-	obs.	14·8	13·4	12·4	11·4	10·7	10·0	9·2	8·8	8·1	0·54
	calc.	14·7	13·4	12·3	11·4	10·6	9·9	9·3	8·7	8·3	±0·01
	obs.	14·5	13·1	12·0	11·1	10·2	9·7	9·0	8·3	8·1	0·58
	calc.	14·6	13·2	12·1	11·1	10·3	9·6	9·0	8·4	8·0	±0·01
Cl^-	obs.	14·8	13·8	12·8	11·9	11·0	10·5	9·9	9·4	9·1	0·45
	calc.	14·9	13·8	12·8	12·0	11·2	10·6	10·0	9·4	9·0	±0·01
	obs.	14·6	13·2	12·4	11·2	10·1	9·6	9·2	8·3	8·3	0·57
	calc.	14·6	13·3	12·2	11·2	10·4	9·7	9·1	8·5	8·1	±0·03

association constants are 0·56 and 0·51 mole^{-1} l. for nitrate and chloride, respectively, with an uncertainty estimated from the spread of the chloride results of ±0·06. The chloride figure appears to confirm the generalisation from other oxidation states that neptunium associates less strongly than plutonium, since 0·67 mole^{-1} l. has been quoted [9] for $PuO_2^+Cl^-$ though the medium was not specified.

Disproportionation of Np^V is thought to be negligible in these solutions. The equilibrium constant for the reaction

$$2NpO_2^+ + 4H^+ = Np^{4+} + NpO_2^{2+} + 2H_2O \qquad (3)$$
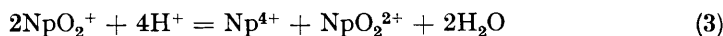
has not been measured for 2M-perchloric acid, but is known for 1M and for the range 5·34—8·67M. Interpolation on a linear plot of log K against acid concentration gave $8\cdot3 \times 10^{-7}$ mole^{-4} l.^{4} for 2M-perchloric acid, which implied that 0·73% of the Np^V can disproportionate. Since neither Np^{IV} nor Np^{VI} associates strongly with chloride or nitrate, the equilibrium disproportionation is unlikely to exceed 1·5% at the highest ligand concentration. With sulphate, however, disproportionation was much greater, so no reliable value could be obtained for the association constant without detailed investigations of various subsidiary equilibria.

The association constants as determined above may include contributions from inner and outer complexes and from long-range medium effects represented by the variation of activity coefficients with composition. They are comparable in magnitude, however, with that for the system $NpO_2^{2+} - Cl^-$ (0·62 mole^{-1} l.; $I = 2\cdot0$; 25°), where medium effects

[9] Katz and Seaborg, " The Chemistry of the Actinide Elements," Methuen, London, 1957, p. 313.

should be similar but where a charge-transfer spectrum is observed over the same range of ligand concentrations.[1]   The absence of charge-transfer spectra with NpO_2^+ and simple anions at wavelengths greater than 230 mµ cannot, therefore, be attributed to the lack of appropriate complexes, but must be due to the low electron affinity of NpO_2^+.   The question of whether anions can affect the ligand field bands of NpO_2^+ is better considered in the light of the results obtained with methanol.

Np^V *in Methanol.*—Fig. 1 shows the two main regions of the spectrum of Np^V in 90% methanol and in water.   In perchlorate solution the ultraviolet band is unchanged from water (open circles) to methanol (full line), thus proving it to be due to an internal transition of the cation NpO_2^+ rather than to solvent–cation charge transfer.   The fact that the ultraviolet band is also unaffected by 1M-chloride in methanol (filled circles) confirms the conclusion that charge transfer is absent for energetic rather than configurational reasons.   The main ligand-field peak of NpO_2^+ in perchlorate solution is shifted from 980 mµ in water to 978 mµ in methanol, with no appreciable alteration in peak height but a decrease in the full width at half-height from 10·0 to 6·5 mµ.   These variations
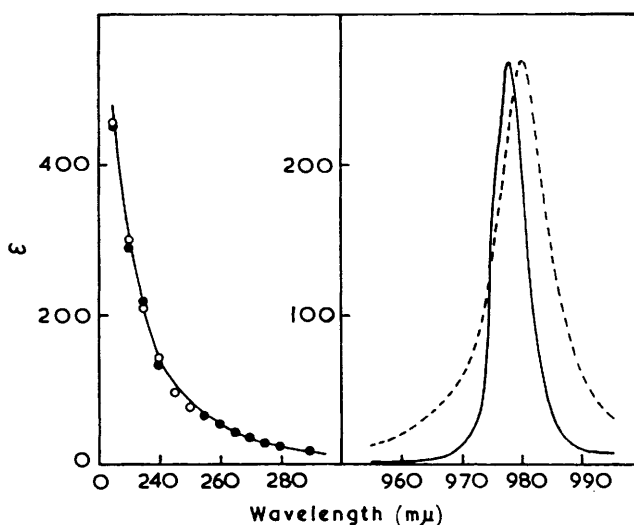

FIG. 1.   Spectrum of Np^V in water and methanol.   Ultraviolet: 1M-HClO$_4$ in 90% methanol —— and in water ○ ; 1M-HCl in methanol ●.   Visible: 1M-HClO$_4$ in water – – – – (width at half-height 10 mµ) and in methanol —— (width at half-height 6·5 mµ).

suggest that the composition of the first solvation shell has, in fact, been changed by 90% methanol, but illustrate how small the ligand-field effects are with this cation.   Chloride in 1M solution has no detectable effect on the 978 mµ band in methanol, so the absence of change in aqueous solution should not be taken as evidence against association.

Np^{IV} *in Water.*—Jørgensen [11] originally attributed the ultraviolet absorption bands of some of the aqueous actinide ions to $5f^n \longrightarrow 5f^{n-1}6d$ transitions, but Ryan and Jørgensen [12] have recently suggested that such transitions of the (IV) state ions lie outside the observable range for all elements beyond uranium.   It can now be shown that the Np^{IV} band is due to solvent–cation charge transfer.

The anion–cation charge transfer ($\pi^2 4 5f^n \longrightarrow \pi^2 3 5f^{n+1}$) band of $NpCl_6^{2-}$ has been located by Ryan and Jørgensen [12] at 33·1 kK with $\varepsilon_{max.} = 2·2 \times 10^3$ and $\delta = 2·1$ kK.   When allowance is made for the difference of 15 kK in optical electronegativity [13] between H_2O and Cl^-, the corresponding band of an aquo-ion of the same co-ordination number is estimated to lie at 48·1 kK (208 mµ).   Although the aquo-ion may have a co-ordination

number as high as 9, any such change is not expected to have a large effect on the transition, and in fact the available data on aqueous Np^{IV} can satisfactorily be interpreted as part of a charge-transfer band with its maximum at 208 mμ. Curve 1 in Fig. 2, which is calculated from $\varepsilon(\text{max.}) = 1.23 \times 10^3$ at 48·08 kκ and $\delta = 4.78$ kκ, adequately represents the experimental points (filled circles) obtained for aqueous perchlorate solutions in the range 230—270 mμ in the present investigation. The large width of the band strongly suggests charge transfer, and there is good evidence that the width cannot be appreciably less than the above estimate, since the extinction coefficient of aqueous Np^{IV} is reported to increase monotonically to 1500 at 230 mμ in 1M-$HClO_4$ by Sjoblom and Hindman [10] and to 1080 at 230 mμ in degassed 0·97M-$HClO_4$ by Jansson.[14] Table 2 shows that the data estimated for the Np^{IV} band are consistent with known values for the analogous charge transfer

TABLE 2.

Solvent–cation charge transfer bands in water and methanol.

Cation	Solvent	$\sigma(\text{max.})$ kκ	$\varepsilon(\text{max.})$	δ (kκ)	Solvent shift (ev)
Np^{IV}	Water	48·1 *	1230 •	4·8 *	1·40
	Methanol	36·8	680	4·6	
Fe^{III}	Water [15]	41·7	4200	4·4	1·66
	Methanol [16] †	28·3	2500	3·8	
Eu^{III}	Water [17]	53·2	285	5·1	1·13
	Methanol [18] †	44·1	270	4·8	

* Estimated as explained in text; all other maxima directly observed. † Perchlorate solution containing not more than 0·2 g. water per litre.

spectra of Fe^{III} and Eu^{III} in aqueous perchlorate solution. The differences in frequency ($\Delta\sigma$) are comparable, when expressed in volts, with those predicted from the differences in formal oxidation potential (ΔE): [19-21] Np^{IV}–Fe^{III}, $\Delta\sigma = 0.79$ v, $\Delta E = 0.59$ v; Eu^{III}–Np^{IV} $\Delta\sigma = 0.633$ v, $\Delta E = 0.59$ v. Other examples of the relationship between charge-transfer spectra and oxidation potentials were discussed at a recent symposium ("Ultraviolet and Visible Spectra of Metal Complexes," Oxford, 1963; see, *e.g.*, Barnes and Day, *J.*, in the press.) The half-widths δ are closely similar for all three cations, and the relative intensities can reasonably be interpreted by supposing that the 5*f* levels are better electron acceptors than the more shielded 4*f*, but not as good as the less shielded 3*d* levels. Further support for these ideas is provided by the effect of substituting the water molecules in the hydration shell of the aquo-ion by methanol and by anions.

Np^{IV} *in Methanol.*—Some oxidation of Np^{IV} to Np^{V} took place in perchlorate solution in this solvent. From the optical density at 978 mμ it was estimated that 47% of the neptunium had been oxidised, and appropriate corrections were made on the basis of the known extinction coefficient of Np^{V} in this solvent. The open circles in Fig. 2 show the ultraviolet spectrum thus obtained for Np^{IV} in perchlorate solution in 90% methanol. The band component of longer wavelength was resolved by applying the Gaussian equation in the form

$$\log_{10} \varepsilon_1/\varepsilon_2 = 0.3010\ \delta^{-2}\ (\sigma_1 - \sigma_2)(2\sigma_0 - \sigma_1 - \sigma_2) \qquad (4)$$

[10] Sjoblom and Hindman, *J. Amer. Chem. Soc.*, 1951, **73**, 1744.
[11] Jørgensen, *Mol. Phys.*, 1959, **2**, 96.
[12] Ryan and Jørgensen, *Mol. Phys.*, 1963, **7**, 17.
[13] Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, London and New York, 1962, p. 94.
[14] Jansson, Ph.D. thesis (London), 1962.
[15] Turner and Miles, *Canad. J. Chem.*, 1957, **35**, 1002.
[16] Stiddard, Ph.D. thesis (London), 1958.
[17] Jørgensen and Brinen, *Mol. Phys.*, 1963, **6**, 629.
[18] Sales, Ph.D. thesis (London), 1961.
[19] McCoy, *J. Amer. Chem. Soc.*, 1936, **58**, 1578.
[20] Cohen and Hindman, *J. Amer. Chem. Soc.*, 1952, **74**, 4679.
[21] Schumb, Sherrill, and Sweetser, *J. Amer. Chem. Soc.*, 1937, **59**, 2360.

where σ_0 is the frequency at the band maximum. With σ_1 corresponding to 285 mμ, δ was calculated for a series of values of σ_2 in the range 300—350 mμ with a trial value of σ_0; σ_0 was then varied until δ was found to be independent of σ_2. Thus curve 2 was obtained with ϵ(max.) = 680 at 36·77 kκ (272 mμ) and δ = 4·57 kκ. It is attributed to charge transfer from methanol to cation, because the peak is displaced from the aquo one by 11·3 kκ or 1·40 ev, which is close to the difference of 1·75 ev in ionisation potential between water and methanol.[4] Table 2 shows that the Np^{IV}–methanol band is closely analogous to those of Fe^{III} and Eu^{III} in methanol, which are displaced from the corresponding aquo-bands by 1·66 and 1·13 ev, respectively. Curve 3 in Fig. 2 was obtained by subtracting curve 2 from the observed extinction coefficient and represents the edge of the next band.

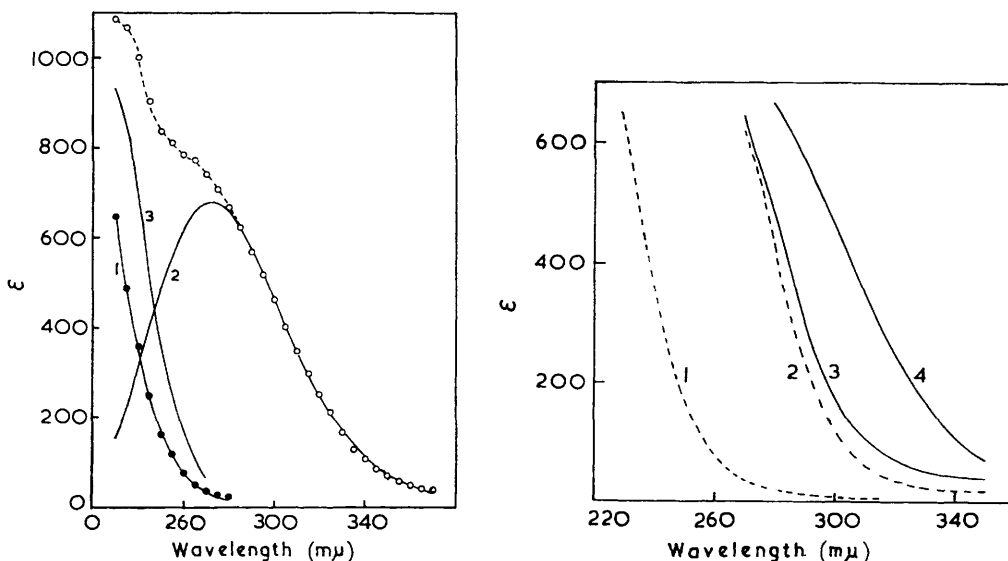The effect of sulphate (Fig. 3) on the ultraviolet spectrum of Np^{IV} is quite different

FIG. 2.   Ultraviolet spectrum of Np^{IV} in 1M-$HClO_4$ in water (●) and in 90% methanol (○).   Curve 1, calc., ϵ_0 = 1230 at 208 mμ (48·08 kκ), δ = 4·78 kκ. Curve 2, calc., ϵ_0 = 680 at 272 mμ (36·77 kκ), δ = 4·57 kκ.   Curve 3, Np^{IV} methanol spectrum — curve 2.

3.   Effect of sulphate on the ultraviolet spectrum of Np^{IV} in water and methanol. 1M-$HClO_4$ in water (curve 1) and in 90% methanol (curve 4).   1M-H_2SO_4 + 0·1M-$HClO_4$ in water (curve 2) and in 90% methanol (curve 3).

when the solvent is methanol (full lines) than when it is water (dotted lines).   Sullivan and Hindman's extraction studies [22] indicate that in the aqueous sulphate solution 91% of the neptunium is in the form of $Np(SO_4)_2$ and most of the rest is $NpSO_4^{2+}$.   In water the band due to $Np(SO_4)_2$ is similar in shape to that of Np^{4+} but is shifted by 6·3 kκ to longer wavelengths, as is understandable if both bands are due to charge transfer.   This shift is comparable with the difference of 8·3 kκ between the charge-transfer peaks of $Fe(H_2O)_6^{3+}$ (240 mμ [15]) and $Fe(SO_4)_2^-$ (300 mμ [23]).   The spectrum of the neptunium–sulphate complex is not much altered by change of solvent from water to methanol, so the main absorbing species is probably the same in both solvents.   Since the effect of sulphate association in methanol is to shift the absorption to shorter wavelengths, and so to decrease the extinction coefficient of Np^{IV} in the range 280—350 mμ, the anions must displace some

[22] Sullivan and Hindman, *J. Amer. Chem. Soc.*, 1954, **76**, 5931.
[23] Whiteker and Davidson, *J. Amer. Chem. Soc.*, 1953, **75**, 3081

of the solvent molecules which are the electron donors in perchlorate solution. Whether substitution occurs in the inner or outer spheres can be estimated from the behaviour of the ligand-field bands.

The visible and near infrared spectra of Np^{IV} in aqueous solution obtained in the present investigation are similar to those of Hindman, Magnusson, and LaChapelle [2] for $1M$-HCl and $1M$-H_2SO_4, but are shown in Fig. 4 (broken lines) for comparison with those for
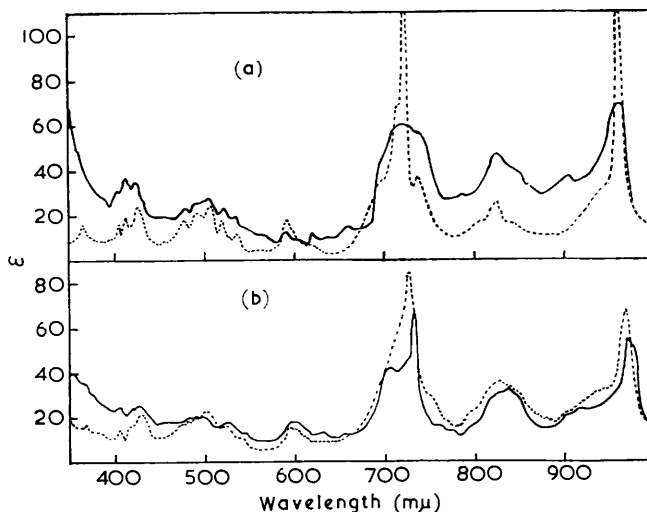

FIG. 4. Effect of sulphate on the visible spectrum of Np^{IV} in water and methanol. (a) $1M$-$HClO_4$ in water (– – – –) and in methanol (———). (b) $1M$-H_2SO_4 + $0\cdot1M$-$HClO_4$ in water (– – – –) and in methanol (———).

methanol (full lines). When water is replaced by methanol in perchlorate solution, absorption is increased slightly in the 400 mμ region by the edge of the ultraviolet band, but the main ligand-field bands at 723 and 960 mμ are considerably broadened with reduction of their peak heights by at least a factor of two. Since chloride in the outer sphere has no detectable effect on these bands,[1] there is little doubt that methanol enters the inner sphere. Sulphate is also thought to compete for the inner sphere in both solvents, since it completely alters the visible spectrum of Np^{IV} in methanolic perchlorate solution and brings it nearly into coincidence with the spectrum of Np^{IV} in aqueous sulphate solution; moreover the latter is quite different from that of Np^{IV} in aqueous perchlorate solution and has previously been taken as evidence for strong complex formation.[2] These qualitative features suggest that the environment of the neptunium must be essentially a sulphate one in both the aqueous and methanolic sulphate solutions, but the quantitative changes which sulphate produces in water are intensified in methanol. This is illustrated by the following extinction coefficient maxima which refer (a) to the aqueous perchlorate solution, (b) to the aqueous sulphate solution, and (c) to the methanolic sulphate solution: (a) 121 * at 723 mμ, (b) 84 at 728 mμ, (c) 68 at 733 mμ; (a) 141 * at 960 mμ, (b) 68 at 968 mμ, (c) 55 at 971 mμ. In the absence of further experimental work, it is uncertain whether these differences are due to a higher proportion of $Np(SO_4)_2$ in methanol or to the formation of a further species such as $Np(SO_4)_3^{2-}$.

Np^{VI} *in Methanol.*—No systematic study of Np^{VI} was made, but when Np^{V} was dissolved in 90% methanolic $1M$-HNO_3 + $0\cdot1M$-$HClO_4$, it was inferred from the decrease in absorption

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* These values may be low on account of the slit-width effect. Hindman, Magnusson, and LaChapelle [2] give 126 at 723 mμ and 160 at 964 mμ for aqueous $1M$-HCl; and 92 at 723 mμ and 75 at 971 mμ for aqueous $1M$-H_2SO_4.

at 978 mμ that 86% of the neptunium had been oxidised to Np^{VI}.   In previous work on aqueous solutions, no formation constant or extinction coefficient could be obtained for a definite NpO_2^{2+}–NO_3^{-} complex, though optical interaction, increasing with cation and anion concentrations and represented by a broad band with a maximum at 328 mμ, was detected.[3]   Stronger association is expected in methanol.   This is confirmed by Fig. 5, which shows what appears to be the first charge transfer band [ε(max.) = 508 at 338 mμ, all the Np^{VI} being assumed associated] observed for a Np^{VI}–nitrate complex, though the number of nitrate ions in the complex is unknown.   The half-width is found to be 3·1 kK from the wavelength at which the peak intensity is halved, but the band is not accurately Gaussian in shape throughout and δ becomes 3·8 kK at longer wavelengths.   Interference by the 14% of the neptunium in the (v) state is unlikely; the corrections made on the basis of the perchlorate spectrum of Np^V did not exceed 6% and Np^V–nitrate charge-transfer is not expected in this region.   Even disproportionation to Np^{IV} and Np^{VI}, if it had occurred
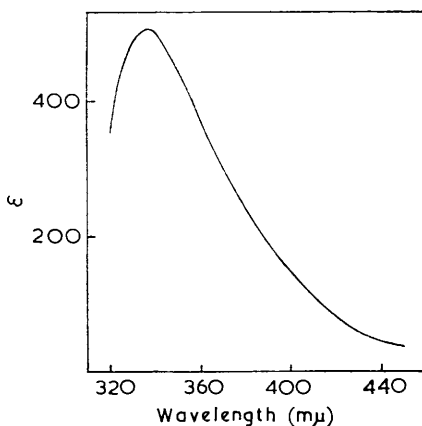

Fig. 5.   Spectrum of Np^{VI} in 1M-HNO_3 + 0·1M-$HClO_4$ in 90% methanol.

to some extent, would not have been optically significant, since the Np^{IV}–nitrate charge-transfer band lies at shorter wavelengths (ε = 270 at 280 mμ [3]).   Stray-light might have caused some error in the vicinity of the peak, since the optical density of the blank is estimated from the spectrum of nitrate ion in methanol [18] to have increased from 0·3 at 340 mμ to 1·2 at 330 mμ and 3·6 at 320 mμ.   More than one nitrate complex may be involved, or there may be some contribution from methanol–cation charge transfer.   It seems certain, however, that the band cannot be due to a perturbation of the nitrate peak at 302 mμ (ε = 7 in methanol [18]) of the type studied by von Halban [24] with non-reducible ions such as Ba^{2+}.   These ions shift the nitrate peak to shorter wavelengths and so cause a decrease in intensity in the region where the present band appears.

EXPERIMENTAL

Neptunium.—[237]Np of purity greater than 99% (0·02% Pu and 0·2% U) was supplied by A.E.R.E., Harwell, and solutions of the desired oxidation state were prepared by the methods developed by Taylor [3] to give adequate purity for ultraviolet spectrophotometry.   Organic impurities were removed by reflux for 3 hr. at 200—250° in a 5 : 4 mixture by volume of 16M-HNO_3 and 72% $HClO_4$.   After a cycle of oxidations and reductions involving hydrazine, nitric acid, and hydroxylamine, Np^V was precipitated with dilute NaOH, washed, and dissolved in 2M-$HClO_4$. Np^{IV} was prepared by hydrogen reduction of Np^V to Np^{III} in 2M-$HClO_4$ in the presence of platinum black at room temperature, followed by air oxidation of Np^{III} to Np^{IV}.   This method avoided the production of any polynuclear species of the readily hydrolysed (IV) state.   Concentrations were determined by α-scintillation counting calibrated with standard Pu and Am sources supplied by A.E.R.E., Harwell.

[24] Von Halban, *Z. Elektrochem.*, 1928, **34**, 489.

Ion Exchange.—0·05 g. of air-dried Dowex 50WX8 resin (100—200 mesh) in hydrogen form was shaken for 12 hr. at 25° with 1 ml. of a 2×10^{-5}M-Np^V solution, containing sufficient perchloric acid and either nitric or hydrochloric acid to give an ionic strength of 2·0 and the desired ligand concentration. Samples of the solution were then counted. Experiments showed that equilibrium with the resin was usually established in 6—8 hours.

Methanol.—Absolute methanol was purified by Sales's method,[18] which gives methanol of optical density 0·05 at 220 mμ in a 1 cm. cell. All Np solutions in aqueous methanol contained 90% of methanol by volume. To 0·05 ml. of 10^{-2}M-Np in aqueous 2M-HClO$_4$ was added methanol containing the appropriate concentration of ligand. All operations, including the filling of the stoppered spectrophotometric cells, were carried out in a nitrogen-swept glove box.

Spectra.—All measurements were made in 1 cm. cells on an Optica CF4 manual, single-beam spectrophotometer against blank solutions containing the same concentrations of all components of the test solution except the Np.

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