

producibile to about 2%. Suitable amounts of borohydride are 4 mg. in 5 ml. of 0.0024 M $[\text{Co}^{1+}(\text{CN})_6]^{3-}$ or 1 mg. in 5 ml. of 0.0003 M .

Acknowledgments.—We are grateful to Mr. J. Bayston of this Division for much of the experimental work and to Dr. J. Barker for help with the

kinetics. In the spectrophotometry we received valuable assistance from several members of the Division of Chemical Physics of C.S.I.R.O., including Dr. J. B. Willis, Dr. N. S. Ham, and Dr. R. N. Beale who carried out the exploratory absorption measurements.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS]

Specific Interaction between Np(V) and U(VI) in Aqueous Perchloric Acid Media¹

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Spectrophotometric, potentiometric and proton relaxation measurements provide evidence for a specific interaction between the oxygenated cations Np(V) and U(VI) in an aqueous acidic media. A value of $K = 0.690 \pm 0.013$ has been calculated for the reaction $\text{NpO}_2^+ + \text{UO}_2^{++} = [\text{NpO}_2^+ \cdot \text{UO}_2^{++}]$ at 25° in perchlorate media, from the spectrophotometric and potentiometric measurements. The reaction also has been studied spectrophotometrically in aqueous chloride media. The improved value of 1.13638 ± 0.00016 abs. v. was determined for the formal potential of the Np(V-VI) couple in 1 M perchloric acid at 25°.

Introduction

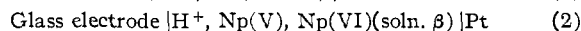
In the course of a study on the kinetics of the reduction of Np(VI) by U(IV),² spectrophotometric observations indicated that there was an interaction between Np(V) and U(VI) ions in an aqueous perchloric acid media. Such an unusual association reaction, *i.e.*, between two different cations in an acidic non-complexing medium, warranted a more detailed investigation. The results of such a study, in which both spectrophotometric and potentiometric methods have been used to establish the existence of a definite complex, are presented in this communication.

Experimental

Reagent Preparation.—Hydrochloric acid solutions were prepared by diluting constant boiling hydrochloric acid with triply distilled water. Sodium chloride solutions were prepared by dissolving recrystallized and dried sodium chloride in triply distilled water. The solution of Np(V) in hydrochloric acid was prepared by dissolving neptunium(V) hydroxide in hydrochloric acid. Conventional radiometric and analytical techniques were used to standardize the solutions. The preparation and standardization of the other reagents employed have been described in a previous publication.²

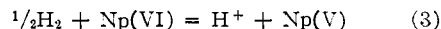
Spectrophotometric Measurements.—Two or five cm. silica absorption cells were filled with a measured volume of a solution containing the sodium or magnesium and uranyl salts plus the appropriate acid. The ionic strength was adjusted to 3.00. Absorption measurements were made from 10,800–9100 Å. with a Carey Model 14 Spectrophotometer. An aliquot of Np(V) solution then was introduced into the cell and the measurements repeated. Measurements on each cell were run in duplicate, and three different cells were used for each uranyl concentration. The average precision was ± 0.003 in the optical density. All measurements were made at 25.0°. No change could be detected in the spectra over a period of ten days.

Potentiometric Measurements.—Potential measurements were made on the independent cell pairs



Except for substitution where necessary in solution α of inert ions of charge +1 and +2, corresponding pairs of cell solutions α and β were formally identical. The e.m.f. of (1)

thus served as a calibration of the glass electrode. Assuming that this calibration potential is the same in solution β , addition of the two potentials (to be referred to as E_α and E_β) yields junction free e.m.f. values corresponding to the reaction



A single Beckman type 39177 glass electrode was used for all measurements. Lightly platinized hydrogen electrodes of the type described by Bates³ were freshly prepared for each determination of E_α . A short spiral of shiny 30 mil platinum wire sealed in soft glass tubing was employed to measure E_β ; this electrode was stored in concentrated nitric acid when not in use. Cell potentials were read to 0.01 mv. using a Leeds and Northrup K-2 potentiometer (with a recently calibrated standard cell) and a Cary Model 31-V Vibrating Reed Electrometer as a null point detector.

The cell proper consisted of a stubby test-tube 28 × 90 mm., which fitted snugly into a cup-shaped glass jacket through which water thermostated at $25.00 \pm 0.01^\circ$ was pumped. A rubber stopper provided support for the electrodes and gas bubbling tubes. Convenient stirring of the cell solution was obtained by resting the entire assembly on top of a magnetic stirrer.

Electro-grade hydrogen was passed through a commercial catalytic purifier, then through a series of several scrubbing towers: dilute sodium hydroxide, dilute perchloric acid, distilled water and finally a sample of solution α immersed in the thermostated water-bath source for the cell jacket. All measurements were carried out in a constant temperature room, $25 \pm 1^\circ$.

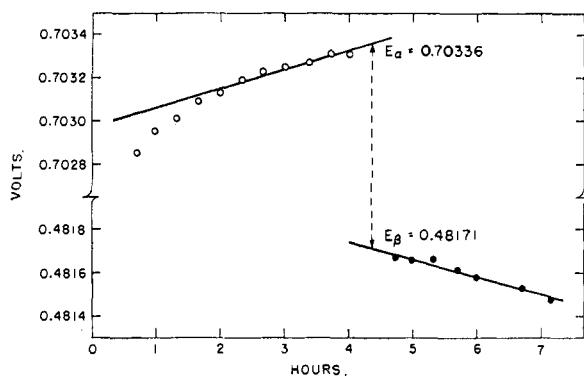
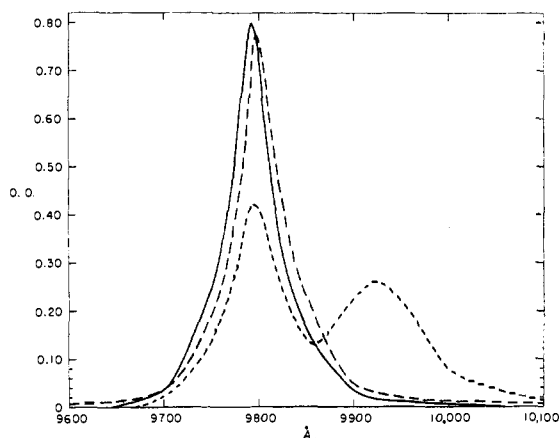
Figure 1 illustrates both the data from a typical run (first entry of Table III) and the procedure employed to obtain the final E_α and E_β values. For each cell pair potential E_α was measured first, the hydrogen electrode requiring from 30 min. to 2 hr. to attain equilibrium. This effect is indicated in Fig. 1 and, of more importance, the continued slow drift in cell potential due to the instability of the glass electrode. From day to day this potential drift varied erratically both in magnitude and direction, but over a period of several hours the change usually could be approximated as linear with time.

After establishment of a satisfactory drift rate for E_α , the glass electrode was carefully rinsed and dried; and the entire procedure was repeated with a fresh tube containing solution β and the appropriately altered electrode assembly for the measurement of E_β . In this change over the sign of the glass electrode is reversed, which ideally should also reverse the slope but not the magnitude of the E_β drift. Addition of the values for E_α and E_β at a common time then yields the potential corresponding to equation 3. In practice any difference in the two drift rates was averaged by use of the

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) J. C. Sullivan, A. J. Zielen and J. C. Hindman, *J. Am. Chem. Soc.*, **82**, 5288 (1960).

(3) R. G. Bates, "Electrometric pH Determination," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 166–167.

Fig. 1.—Variation of E_α and E_β .Fig. 2.—Absorption spectra of Np(V) in HClO_4 , —; HCl — —, $\text{HClO}_4\text{-UO}_2(\text{ClO}_4)_2$, - - -.

mid-point between the last and first of the two cell readings as the common extrapolation point.

This procedure minimized the commonly observed eccentric behavior of the glass electrode. The precision of the final potentials ranged between 0.05–0.10 mv.

Relaxation Time Measurements.—The proton spin relaxation times were measured at 40 mc. using "spin-echo" procedures that will be described in detail in a later manuscript. Temperature was maintained at 25° for these measurements.

Results and Discussion

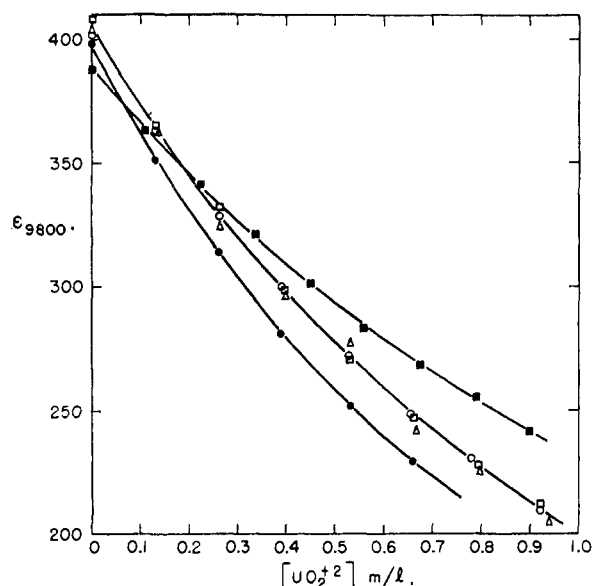
The vibronic⁴ transitions in the absorption spectra of Np(V) in aqueous solution are not appreciably affected by changing the anionic composition from three molar perchlorate to three molar chloride. In particular the intense band centered at ca. 9800 Å. exhibits only a so-called "medium" effect (see Fig. 2) similar to that described by Newton⁵ for the Pu(VI) band at 8300 Å.

This effect can be explained qualitatively if one postulates small changes in the vibrational energy of interaction between the Np(V) and coordinated water molecules. By implication (from the spectra in Fig. 2) the symmetry of the field surrounding the cation remains invariant when chloride ion is substituted for perchlorate ion in the solution. Therefore one is unable to ascribe the small changes observed to complex ion formation.

If in a solution of Np(V) containing perchloric acid we replace sodium or magnesium perchlorate

(4) Similar transitions for U(IV) are discussed by R. Satten, D. Young and D. M. Gruen, *J. Chem. Phys.*, **33**, 1140 (1960).

(5) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **61**, 934 (1957).

Fig. 3.—Variation of E_{9800} with $[\text{UO}_2^{2+}]$: \circ , set A; \square , set B; \triangle , set C; \bullet , set D; \blacksquare , set E. See Table I for identification.

with uranyl perchlorate, the band at 9800 Å. decreases in intensity and a new band centered at 9925 Å. appears (Fig. 2). A change in symmetry of the crystal field surrounding the Np(V) ion with the concomitant change in the electronic energy levels of this ion can give rise to the observed change in spectrum. Such evidence is generally considered to be a sufficient condition to establish the existence of a complex ion.

However, since the transitions of the Np(V) ion are not described quantitatively by theory, it was deemed advisable also to obtain evidence based upon some other type of measurement in order to verify the existence of this cation-cation complex. We have therefore also studied the potential of the Np(V)–Np(VI) couple in the presence of varying amounts of uranyl ion using a novel technique that eliminates junction potentials.

A. Spectrophotometric Studies.—The variation of ϵ ($\epsilon = d/lc$ where d is the optical density, l the path length in cm. and c the total concentration of Np(V) in mole/l.) with uranyl concentration is presented graphically in Figs. 3 (9800 Å.) and 4 (9925 Å.).

At both wave lengths the data are described adequately by the usual expression

$$\epsilon = (\epsilon_0 + \epsilon_1 K[\text{U(VI)}]) / (1 + K[\text{U(VI)}]) \quad (4)$$

where ϵ_0 is the molar extinction coefficient of Np(V), $K = [\text{Complex}] / [\text{Np(V)}][\text{U(VI)}]$ and we defer identification of the parameter ϵ_1 until later.

The weighted⁶ least squares adjustment of the data in terms of (4) was carried out on an IBM 704 using a generalized least squares program developed by the Applied Mathematics Division of this Laboratory. The results of the calculations

(6) The weighting factor arises only from the functional relationship since the precision in the measured optical densities was the same for all observations.

TABLE I

Set	[H ⁺]	[Np(V)] × 10 ³	Added salt	SUMMARY OF LEAST SQUARES ADJUSTMENTS OF SPECTROPHOTOMETRIC DATA, 25.0°, μ = 3.00					
				ε ₁	ε ₂	K	ε ₁	ε ₂	K
A	0.114	1.003	Mg(ClO ₄) ₂	405 ± 2	-107 ± 31	0.67 ± 0.08	12 ± 1	324 ± 38	0.66 ± 0.07
B	.114	1.024	NaClO ₄						
C	.103	0.296 ^a	NaClO ₄						
D	.992	1.008	Mg(ClO ₄) ₂	397 ± 3	-106 ± 58	.76 ± .17	12 ± 1	349 ± 66	.70 ± .13
E	.111	1.071	NaCl	388 ± 2	-98 ± 42	.48 ± .08	14 ± 2	326 ± 97	.44 ± .12
E ^b	.111	1.071	NaCl	387 ± 1	123 ± 21	3.4 ± .3	14 ± 2	177 ± 34	3.3 ± .6

^a Mean value, actual range 0.2763 - 0.3161 × 10⁻³ M. ^b Correcting [UO₂⁺⁺] assuming UO₂⁺⁺ + Cl⁻ = UO₂Cl⁺, K = 1.

are presented in Table I with the 95% confidence limits listed as uncertainties.

From the graphical presentation of the data a comparison of sets A and B (Figs. 3 and 4) demonstrates that the change in ε is independent of the total perchlorate ion concentration. This is apparent since both sets of experiments were run under conditions of constant ionic strength, but when sodium perchlorate is used to maintain the ionic strength, there is a change in the total perchlorate ion concentration of from three molar to two molar.

Set C demonstrates that a threefold change in concentration of Np(V) does not affect the variation of ε with uranyl concentration.

Set D indicates an apparent variation in these systems on increasing the hydrogen ion concentration by a factor of approximately 10.

Consequently in Table I we have presented the results of a separate calculation for set D while combining sets A, B and C in the adjustment of the data, according to equation 4.

Inspection of the results tabulated in I indicates that there is no significantly different value for K from these four sets of data and consequently the composition of this complex is solely a one to one complex of uranyl ion (hydrated) and Np(V) ion (hydrated).

The negative value for ε₁ at 9800 Å. obviously precludes the interpretation of that parameter as the molar extinction coefficient of the complex at that wave length. Such a result could conceivably arise from one or more of the factors that have previously been discussed in detail.⁵ To demonstrate that the negative value of this parameter is not a reflection of an improper functional form, we have carried out these calculations.

If it is assumed that two complexes are formed equation 4 takes the form

$$\epsilon = \frac{\epsilon_0 + \epsilon_1 K_1 [U(VI)] + \epsilon_2 K_2 [U(VI)]^2}{1 + K_1 [U(VI)] + K_2 [U(VI)]^2} \quad (5)$$

Preliminary estimates of K₁ and K₂ were obtained from the 9800 Å. data by assuming ε₁ = ε₂ = 0, and these quantities in turn provided estimated values of ε₁ and ε₂ at 9925 Å. The least squares program then calculated corrections to these estimates, yielding finally independent values for all parameters at each wave length. For the combined sets A-C at 9800 Å. the only positive parameters obtained were ε₀ and ε₂K₂, and for the 9925 Å. data all parameters were negative except ε₀. This clearly demonstrates that increasing the number of species postulated is not the rationale of the negative ε₁ values tabulated.

Since the values of K computed for the same data at both wave lengths are consistent with the concept that a single complex is formed between the U(VI) and Np(V) ion, a tenable hypothesis is that ε₁ at 9800 Å. is actually a function of the uranyl ion concentration.

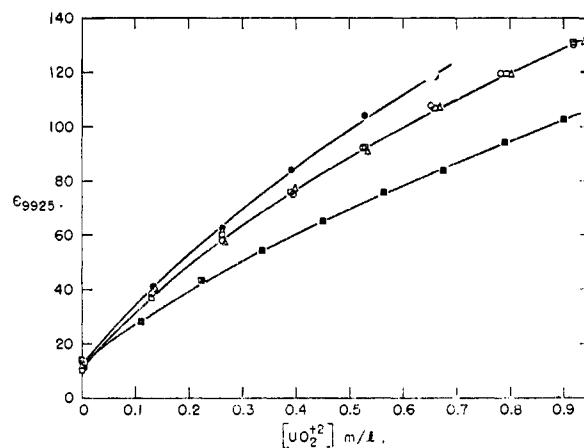


Fig. 4.—Variation E_{9925} with $[UO_2^{2+}]$ —same code as Fig. 3.

The results obtained in a series of experiments in which the anion used was the chloride ion are presented graphically in set E (Figs. 3 and 4). It is apparent that uranyl chloride solutions exert a less marked effect on the Np(V) spectra than do the perchlorate solutions of the same molarity.

Calculation of the parameters, in terms of equation 4, for set E are presented in Table I. If we assume no complexing of the uranyl ion by chloride ion, the values for the association quotient are smaller than those obtained in perchlorate systems. This difference is hardly surprising since the appropriate activity coefficient ratios which we have neglected should differ going from perchlorate to chloride solutions.

If, however, we attempt to correct the uranyl ion concentration for the effect of chloro complexing using an estimated value of 1⁷ for the association constant, we obtain values for the parameters quite inconsistent with the results obtained for the perchlorate systems. Since there is uncertainty as to the extent of chloride complexing of the uranyl ion^{5,7} and because of the results obtained upon the assumption of such complexing, we feel that the first results are the more reasonable values for the parameters in the chloride system.

(7) R. A. Day and R. M. Powers, *J. Am. Chem. Soc.*, **76**, 3895 (1954).

Further evidence that the anion does not play a predominant part in the formation of this complex is provided by observations made by Keder,⁸ who demonstrated that uranyl nitrate added to a solution of Np(V) in nitric acid solutions causes a decrease of the 9800 Å. band and the growth of a new band centered at *ca.* 9930 Å. In addition he observed that the spectrum of Np(V) was the same in an almost saturated solution of calcium nitrate as it was in a two molar solution of nitric acid.

A number of additional observations were made in an effort to determine how general is this phenomenon of complex ion formation between oxygenated cations in perchloric acid solutions.

No change in the spectrum of Np(V) was observed up to concentrations of *ca.* 0.5 *M* in Np(V). Addition of 0.4 *M* V(IV) caused no change in the Np(V) spectrum. A spectral change similar to that discussed was observed in a solution 0.44 *M* Np(VI).

Pu(VI), which is isoelectronic with Np(V), has a strong absorption band at *ca.* 8300 Å. This band was not found to be affected by uranyl perchlorate up to a concentration of three molar.

These observations lead to the hypothesis that we can probably expect interaction between the oxygenated cations of the actinides only if the product of the formal charges does not exceed two and the total number of 5f electrons does not exceed three.

B. Potentiometric Studies.—Both as a test of our experimental technique and as a preliminary to the interpretation of the effect of uranyl ion, it was necessary to demonstrate that known changes in the Np(V)–Np(VI) ratio adequately correlate with the observed cell potentials. Accordingly a series of measurements were carried out employing the cell pairs: solution $\alpha = 0.961 M HClO_4, 1.052 \times 10^{-2} M NaClO_4$ and $0.955 \times 10^{-2} M Zn(ClO_4)_2$; solution $\beta = 0.961 M HClO_4, (1.052 \times 10^{-2} - A) M NaClO_4, A M NpO_2ClO_4, (0.955 \times 10^{-2} - B) M Zn(ClO_4)_2$ and $B M NpO_2(ClO_4)_2$. The concentration ratio *A/B* of the neptunium ions was varied over a ninefold range; however, the total neptunium concentration was kept constant (within 2%) at $1.01 \times 10^{-2} M$.

The neptunium ion ratio was determined by direct spectrophotometric analysis of β solution samples at the end of each potential determination. The Np(V) concentration was determined using the 9800 Å. absorption band, Np(VI) then was reduced to the (V) state by addition of excess hydrogen peroxide to the same absorption cell and the measurements repeated. Triplicate determinations of each of three independent samples were made for each potential run.

At one atmosphere of hydrogen the cell potential corresponding to equation 3 is given by

$$E = E^0 - E_\gamma - RT/F \ln [H^+][Np(V)]/[Np(VI)] \quad (6)$$

where *E* is the observed e.m.f., *E*⁰ the standard potential of the Np(V–VI) couple and *E*_γ the composite contribution of all pertinent activity coefficient terms. At 25° and letting *R* represent the ratio $[Np(V)]/[Np(VI)]$, the formal electrode potential *E'* is

(8) Private communication from W. E. Keder, Hanford Laboratories, Richland, Wash.

$$E' = E^0 - E_\gamma = E + 0.059156 \log R [H^+] \quad (7)$$

A summary of the results is presented in Table II. All *E*_α entries have been corrected to a standard atmosphere of hydrogen; these values therefore represent what may be considered the standard potential of the glass electrode plus correction terms for the asymmetry potential and any deviation from the *RT/F* slope. The variation of *E*_α is not extreme in this series, but abrupt changes sometimes amounting to one mv. have been observed and emphasize the need of calibrating the glass electrode immediately prior to the *E*_β measurement.

TABLE II
FORMAL POTENTIAL OF THE Np(V–VI) COUPLE AT 25.00°
[H⁺] = 0.961 *M*; μ 1.000

R	<i>E</i> _α , v.	<i>E</i> , v.	<i>E'</i> , v.
0.3829	0.70365	1.16235	1.13666
0.6749	.70363	1.14743	1.13630
1.113	.70368	1.13458	1.13631
1.834	.70381	1.12174	1.13630
2.438	.70380	1.11440	1.13627
3.346	.70394	1.10654	1.13654

The constancy of the tabulated values for *E'* indicates that equation 7 adequately represents the data. The scatter is attributed primarily to the determination of the Np(V)–Np(VI) ratio, which becomes increasingly more inaccurate as *R* differs from unity. Weighting the *E'* values on the basis of optical density errors in *R* as the determining source of uncertainty, the weighted mean and 95% confidence level of the formal potential in 1 *M* perchloric acid was found to be 1.13638 ± 0.00016 abs. v. This analysis gave the reasonable value of 0.0010 for the corresponding standard deviation of the mean optical density readings.

In one molal perchloric acid Cohen and Hindman⁹ report 1.1373 ± 0.0010 v. for the formal potential. Converting to the mole/l. concentration scale,¹⁰ this value becomes 1.1361 ± 0.0010 v. The agreement is excellent and in addition our new value of the formal potential represents a considerable decrease in the uncertainty level.

Measurement of the effect of uranyl ion on the Np(V)–Np(VI) couple was carried out in solutions corresponding to sets A–C of Table I. The cell pairs consisted of: solution $\alpha = 0.1000 M HClO_4, 0.9650 M Mg(ClO_4)_2, 5.055 \times 10^{-3} M NaClO_4$; solution $\beta = 0.0997 M HClO_4, (0.9604 - C) M Mg(ClO_4)_2, C M UO_2(ClO_4)_2, 5.11 \times 10^{-3} M NpO_2ClO_4$ and $4.94 \times 10^{-3} M NpO_2(ClO_4)_2$.¹¹ The concentration of uranyl covered the range from zero to complete replacement of the magnesium. In order to hold the neptunium oxidation state ratio as constant as possible, the same stock solution of mixed Np(V)–Np(VI) was employed for

(9) D. Cohen and J. C. Hindman, *J. Am. Chem. Soc.*, **74**, 4679 (1952).

(10) One molal = 0.9546 *M* HClO₄ at 25° on the basis of a Stirling's interpolation of the density data of A. E. Markham, *ibid.*, **63**, 874 (1941).

(11) Note that there are some small discrepancies in matching the make up of the two solutions, especially in H⁺. However, this should not affect the results since *E*_α is insensitive to changes in hydrogen ion concentration. The cancellation of hydrogen ion activity is the principal advantage of using the cumbersome hydrogen electrode as a calibration source.

all runs. Some variation in the ratio still occurs due to α particle reduction of the Np(VI).¹²

Assuming the formation of a single complex (equation 4) it is readily shown that the complete e.m.f. equation is

$$E = E^0 - E_\gamma - RT/F \ln \mathbf{R}[\text{H}^+]_{a_w(\beta)}/a_w(\alpha)(1 + K[\text{UO}_2^{++}]) \quad (8)$$

where a_w is the water activity and all other symbols are as defined before with the distinction that \mathbf{R} in (8) indicates $\Sigma[\text{Np(V)}]/\Sigma[\text{Np(VI)}]$ and not the concentration ratio of the free ions. Inclusion of the a_w ratio represents a minor correction—unnecessary in equation 7—due to the small variation of the water activity as Mg^{++} is replaced by UO_2^{++} . A discussion of the water activity effect is presented by Dole.¹³

Modifying the E' of equation 7 with the a_w correction, we obtain the final results at 25°

$$E' = E + 0.059156 \log \mathbf{R}[\text{H}^+]_{a_w(\beta)}/a_w(\alpha) \quad (9)$$

$$E' = E^0 - E_\gamma + 0.059156 \log (1 + K[\text{UO}_2^{++}]) \quad (10)$$

Following the same procedure as with equation 4, the least squares adjustment of the data yielded the following values and 95% confidence limits of the parameters: $K = 0.691 \pm 0.013$ l./mole and $E^0 - E_\gamma = 1.12681 \pm 0.00012$ abs. v.

The data and results are presented in Table III with $E'_{\text{calcd.}}$ corresponding to points on the least squares adjustment of equation 10. The quantity $[\Sigma\text{U}]$ indicates the total uranyl concentration and must be corrected for the small fraction complexed before application in equation 10. The \mathbf{R} values represent the smooth curve results of a series, carried out over a 3 week period, of spectrophotometric analyses of the Np(V)–Np(VI) ratio in the mixed stock solution. The water activity ratios in the α and β solutions were calculated by linear interpolation from osmotic coefficient data for pure 1 *M* magnesium and uranyl perchlorates.¹⁴

TABLE III
EFFECT OF URANYL ON THE Np(V–VI) POTENTIAL
[H⁺] = 0.0997 *M*; μ = 3.00; t = 25.00°

$[\Sigma\text{U}]$, moles/l.	\mathbf{R}	$\frac{a_w(\beta)}{a_w(\alpha)}$	E , v.	E' , v.	$E'_{\text{calcd.}}$, v.
0	1.036	1.0000	1.18507	1.12674	1.12681
0	1.032	1.0000	1.18531	1.12688	1.12681
0.1921	1.032	0.9975	1.18850	1.13003	1.13001
.3842	1.033	.9950	1.19130	1.13277	1.13285
.5762	1.034	.9925	1.19407	1.13551	1.13540
.7683	1.037	.9900	1.19629	1.13773	1.13773
.9604	1.035	.9875	1.19850	1.13983	1.13987

In the calculation of K by equation 10 it has been tacitly assumed that there is no interaction between uranyl ion and Np(VI). No experimental evidence for any such interaction has been found. The broad Np(VI) absorption band centered at ca. 12235 Å. is somewhat distorted in the presence of high concentrations of uranyl ion; but since Mg(II) was observed to produce a similar broadening of the band, this can be interpreted as

(12) A. J. Zielen, J. C. Sullivan and D. Cohen, *J. Inorg. and Nuclear Chem.*, **7**, 378 (1958).

(13) M. Dole, "The Glass Electrode," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 276.

(14) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press, Inc., New York, N. Y., 1959, pp. 486, 488.

a medium effect.⁵ Also if interaction between Np(VI) and uranyl does occur, the net effect would be a decrease in the K determined potentiometrically over the value determined from the spectrophotometric results, the amount depending on the relative complexing of the two neptunium ions. Clearly this is not the case.

Other assumptions implicit in the use of equation 10 involve, despite constant ionic strength, neglect of the gross medium change produced by substitution of UO_2^{++} for Mg^{++} . Any effect on the concentration "constant" K is common to both the spectrophotometric and potentiometric determinations; however, the calculated K 's would differ if E_γ in (10) varies appreciably. The assumption that medium changes have a negligible effect on the calibration potential E_α remains a moot point.

C. Relaxation Measurements.—The proton spin relaxation times T_1 and T_2 are known to be markedly influenced by the addition of paramagnetic ions to water. Then, changes in these relaxation times with changing solution composition provides a method for observing the effective concentration of the paramagnetic ion and can thus be used as a measure of complex ion formation.¹⁵

We have therefore examined the effect of the Np(V) ions, for a few solutions of varying uranyl concentration on proton spin relaxation times. The results are presented graphically in Fig. 5.

Before examining these results it should be pointed out that the residual paramagnetism of the uranyl ion affects T_1 and T_2 . $NT_1 = 0.842$ *M* sec. and $NT_2 = 0.346$ *M* sec. The corresponding values for Np(V) are 2.42×10^{-4} and 1.72×10^{-4} *M* sec., respectively, which indicates quite conclusively that in the solutions examined we can neglect the effect of U(VI) on the observed relaxation times. The ratio $T_1/T_2 = 2.4$ for U(VI) very probably is caused by the same factor that gives rise to the residual paramagnetism, the "high frequency terms" or off-diagonal elements of the magnetic moment operator.¹⁶

The variation of the ratio T_1/T_2 from unity for Np(V) could very well arise for the same reason although a contribution to T_2 from scalar coupling between the proton and the unpaired electrons of the Np ion is possible.¹⁷

The decrease of T_1 with increased U(VI) concentration implies that the interaction between that ion and Np(V) does not quench the effective moment of the latter. In addition if the dipolar contribution to T_2 is assumed to be approximately equal to T_1 , there must be an additional contribution to T_2 caused by spin exchange interaction.

As has been pointed out¹⁸ this type of effect can be caused by either chemical exchange of the coordinated water (or proton exchange) or by a change in the quantization of the electron spin.

The assumption of a change in the spin-orbit coupling would be consistent with the observation

(15) See for example, L. O. Morgan, J. Murphy and P. F. Cox, *J. Am. Chem. Soc.*, **81**, 5043 (1959).

(16) J. C. Eisenstein and M. H. L. Pryce, *Proc. Royal Soc. (London)*, **A229**, 20 (1959).

(17) N. Bloembergen, *J. Chem. Phys.*, **27**, 527 (1957).

(18) R. A. Bernheim, T. H. Brown, H. S. Gutowsky and D. E. Woessner, *ibid.*, **30**, 950 (1959).

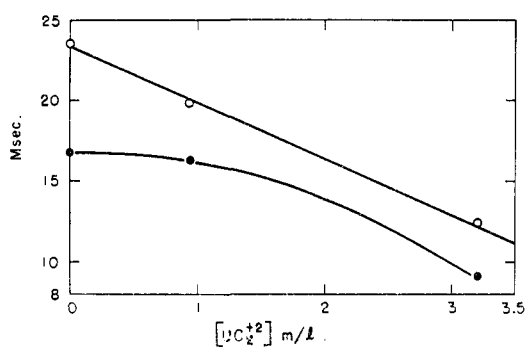


Fig. 5.—Proton spin relaxation times for Np(V) ions 25°, 40 megacycles: ○, T_1 ; ●, T_2 ; $1.03 \times 10^{-2} M$ Np(V) ca. $0.1 M$ HClO₄; $[UO_2^{2+}] = 0$, $\mu = 3.0$ Mg(ClO₄)₂.

on T_1 and T_2 . The paucity of the data does not warrant any more extended discussion of possible details of the ionic interactions, but it is to be em-

phasized that the observations are indicative of specific interaction between the Np(V) and uranyl ions.

Conclusion

Three separate types of measurements are consistent with the concept of specific interaction between the Np(V) and uranyl ions in acid solution. No evidence has been obtained for the participation of anions in this complex.

The association quotient determined by spectrophotometric and potentiometric methods agrees within the limits of error despite the drastically different assumptions made in the two types of measurements. Weighting the individual determinations (perchlorate solutions only) according to their listed uncertainties, we obtain a final weighted mean value for the association quotient at 25° and ionic strength of three; $K = 0.690 \pm 0.013$ l./mole.

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Reactions of Permanganate Ion with Borohydride Ion

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The reactions between BH_4^- and MnO_4^- in basic solutions were investigated. The products of the reaction were shown to include BO_2^- , MnO_4^- , MnO_2 and H_2 . Interestingly, all the H_2 was shown to originate from the BH_4^- . The second-order specific rate constant was found to be 2×10^3 l./mole-sec. at 20°. The proposed mechanism involves hypomanganate.

Introduction

On mixing basic solutions of borohydride and permanganate ions the following was observed: first the solution was pink (MnO_4^-), then grey or colorless (at about equal concentrations of MnO_4^- and MnO_4^- the visible absorption spectrum is almost flat since the absorbancies of the two species complement each other), then green (MnO_4^-) and much later yellow-brown (MnO_2). These color changes varied with the order of mixing. If BH_4^- was added to MnO_4^- , the following sequence was seen: pink, grey, green and then yellow-brown. If the reverse addition was used the pink persisted for a longer time, instead of grey the solution looked colorless, and the solution did not get as intensely green before turning yellow-brown. This paper reports a study of these reactions.

Extensive studies of the reducing properties of borohydride ion toward organic oxidants have been published.¹ However, relatively few reactions^{2,3} of BH_4^- with inorganic species have been intensively investigated. Permanganate oxidations of inorganic ions in basic solution resulting in MnO_4^- have been investigated,⁴ but only in a few cases are the kinetics known.⁵⁻⁸ Jensen⁹ was the first to

study the BH_4^- reduction of MnO_4^- ; he investigated this reaction as a basis for a quantitative potentiometric titration.

We became interested in this reaction for two reasons. First, it is an oxidation of analytical interest occurring in strongly basic solution in contrast to the iodometric⁹ or gas evolution⁹ methods which are performed in acid solution. Second, the rate of reaction⁸ approaches the speed of the "electron transfer" reaction¹⁰ between permanganate and manganate.

Experimental

The reactions of BH_4^- in basic solutions were examined with initial concentrations of BH_4^- from 0.002 to 500 mM, of MnO_4^- from 0.02 to 500 mM and in OH^- from 10 to 200 mM. The ratio of initial concentrations of MnO_4^- to BH_4^- after mixing was varied from 0.5:1 to 33:1. The effect of the order of mixing was investigated. For convenience, the discussion of the experiments has been divided into the following: (a) gas evolution, (b) spectrophotometry, (c) potentiometry, (d) chemical analysis by separation and (e) kinetics.

(a) **Gas Evolution.**—In base concentrations from 0.05 to 0.2 M the addition of 0.4 M MnO_4^- to 0.04 M BH_4^- or the reverse liberated only one gas, H_2 . An experiment using borohydride in heavy water showed that all the hydrogen liberated is derived from the hydridic hydrogens of the borohydride ion.

The volume of H_2 gas evolved was followed as 0.15 M MnO_4^- was added in dropwise increments to 0.5 M BH_4^- in 0.1 M OH^- . Each addition of MnO_4^- evolved 0.33 of moles H_2 per mole of MnO_4^- , until 2.3 moles of MnO_4^- had been added per mole of BH_4^- , after which no more H_2

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