Table II. Magnetic and Spectroscopic Properties of the $CsNiX_3$ Salts

Compd	Ni-Ni distance, Å	Θ, deg	μ_{eff}, BM	Δ, cm^{-1}
$CsNiF_3$	2.61[a]	+8[b]	3.6[b]	--
$CsNiCl_3$	2.96[c]	−76,[d,e] −69[f]	3.37,[d] 3.41[f]	6950[g]
$CsNiBr_3$	3.12[h]	−101[d]	3.42[d]	6550[g]
$CsNiI_3$	3.38[i]	−250[j]	3.6[j]	6500[j]

[a] D. Babel, *Z. Anorg. Allg. Chem.*, **369**, 117 (1969). [b] Reference 10. [c] G. N. Tishchenko, *Tr. Inst. Kristallogr. Akad. Nauk SSSR*, **11**, 93 (1955). [d] Reference 12. [e] Reference 14. [f] Reference 13. [g] G. L. McPherson and G. D. Stucky, *J. Chem. Phys.*, **57**, 3780 (1972). [h] G. D. Stucky, S. D'Agostino, and G. McPherson, *J. Amer. Chem. Soc.*, 88, 4828 (1966). [i] Reference 2. [j] This work.

the nickel-nickel separations are rather short (2.6-3.4 Å) and each nickel(II) ion shares three halide ions with the neighboring nickel(II) ions. Thus, both direct (through space) and indirect (through ligand) magnetic interactions are possible. On the other hand, the separations between adjacent nickel(II) ions in different chains are considerably larger (6.2-8.0 Å), and there are no bridging ligands. Clearly, the intrachain interactions should be much stronger than the interchain interactions. This has been shown to be true for $CsNiF_3$[10,11] and $CsNiCl_3$[12-15] by magnetic susceptibility and neutron diffraction studies.

Direct exchange interactions are very dependent on interionic separations while indirect exchange is dependent on the degree of covalency in the metal-ligand-metal linkage. Considering the $CsNiX_3$ series, one would expect the direct effects to decrease going from fluoride to iodide, since the Ni-Ni separation increases from 2.6 to 3.4 Å. In contrast the opposite trend would be expected for indirect exchange, since covalency presumably increases going from fluoride to iodide. On the basis of these considerations, the magnetic data suggest that indirect exchange is responsible for the magnetic properties of $CsNiCl_3$, $CsNiBr_3$, and $CsNiI_3$. This conclusion is quite reasonable for systems containing d^8 ions such as nickel(II), since the unpaired electrons occupy the e_g orbitals which are directed toward the ligands. The fact that $CsNiF_3$ is ferromagnetic is somewhat surprising. It is possible that direct rather than indirect exchange is dominant in this material. A second possibility is that the indirect exchange in $CsNiF_3$ leads to ferromagnetic rather than antiferromagnetic coupling. Indirect exchange is known to be quite sensitive to the metal-ligand-metal angle, and the Ni-F-Ni angle in $CsNiF_3$ is somewhat larger (80°) than the Ni-Cl-Ni angle in $CsNiCl_3$ (75°). The Goodenough-Kanamori rules predict ferromagnetic coupling in systems where the metal-ligand-metal angle is 90°.

Acknowledgment. We wish to acknowledge Tulane University for the support of this work.

Registry No. $CsNiI_3$, 38496-65-0; NiI_2, 13462-90-3.

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(11) M. Steiner, *Solid State Commun.*, 11, 73 (1972).

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Oak Ridge, Tennessee 37830

Comparative Solution Chemistry, Ionic Radius, and Single Ion Hydration Energy of Nobelium[1]

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Received February 12, 1974

AIC400938

The chemistry of nobelium has been examined by comparing its behavior with other elements in solvent extraction and ion-exchange systems, by confirming that its normal valence is 2+ by acid dependence of its solvent extraction behavior, by derivation of its ionic radius using both experimental and theoretical methods, and by calculation of the single ion heat of hydration. In the experimental work about 500-1000 atoms per experiment of cyclotron-produced ^{255}No ($T_{1/2}$ = 223 sec) were used. Its extraction behavior in a tri-*n*-octylamine-HCl system was compared with that of divalent mercury, cadmium, copper, cobalt, and barium and it was found to be most similar to the relatively noncomplexing alkaline earths. Comparison to the alkaline earths in a cation-exchange resin-HCl system indicated it to be most like Ca^{2+} and comparison with these elements in a bis(2-ethylhexyl)phosphoric acid (HDEHP) liquid-liquid extraction system showed nobelium to have an extraction behavior between that of Ca^{2+} and Sr^{2+}. The extraction of nobelium into HDEHP as a function of pH allowed a direct determination of the valence as 2+ in confirmation of previous indications. The ionic radius of No^{2+} was estimated from a linear correlation of ionic radius with distribution coefficient for several divalent ions. A value of 1.0 Å was obtained from ion-exchange data and 1.1 Å from liquid-liquid extraction data with theoretical calculations giving a value of 1.1 Å. The single-ion heat of hydration, obtained from a Born type calculation, was −355 kcal (g-atom)$^{-1}$.

Introduction

The work of Maly, Sikkeland, Silva, and Ghiorso[4] showed nobelium to be most stable in acid aqueous solutions in an oxidation state lower than the 3+ state of its neighbors in the actinide series. Their experiments indicated the behavior of nobelium to be consistent with a 2+ state that could be expected to be stabilized by a $5f^{14}$ electron configuration in the No^{2+} ion. Subsequent work by Silva, Sikkeland, Nurmia, Ghiorso, and Hulet[5] assumed the 2+ state for nobelium in acid aqueous solution and determined a No^{3+}-No^{2+} reduction

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(3) Chemical Development Section A, ORNL Chemical Technology Division.

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potential of +1.4–1.5 V. The present work further characterizes the behavior of nobelium in solution and confirms the 2+ valence as the normal oxidation state. In order to begin an understanding of nobelium chemistry based on thermodynamics, we further obtain a value of the ionic radius and calculate the single ion hydration energy from it.

Experimental Section

Nobelium Production. Nobelium-255 ($T_{1/2} = 223 \pm 11$ sec)[6] was made at the Oak Ridge Isochronous Cyclotron (ORIC) by the ^{249}Cf(^{12}C,α2n) reaction. The ^{12}C beam at an energy of 73 MeV and an intensity of 3×10^{12} particles/sec allowed a production rate of about 280 ^{255}No atoms/min. The atoms were deposited on an aluminum "rabbit" by a gas jet. About 1200 atoms (after decay during collection) were transferred to the laboratory every 10 min by pneumatic tube. The ^{249}Cf target, the gas-jet system used for collecting the nobelium atoms on the rabbit, and the pneumatic system for transferring the rabbit from the beam room to the laboratory have been described elsewhere.[7]

The aluminum rabbits were anodized and then heated to 400 or 500° to make them chemically resistant to the acids employed to remove the ^{255}No atoms for subsequent experimentation. Because of losses due to radioactive decay during the chemistry and to chemical losses and to the counting geometry of about 30%, usually only about 20% of the atoms delivered to the laboratory were counted in the solvent extraction experiments and only about 3% in the column experiments.

Counting. The detection of the nobelium was carried out by α-particle energy analysis. The α counting was done with Si(Au) surface barrier detectors of area 200 mm^2. The energy resolution of less than 50 keV was more than sufficient to separate the 8.11-MeV α group used for analyzing the No from those of the only interference of importance [^{250}Fm ($T_{1/2}$ = 30 min, E_α = 7.44 MeV; produced by the reaction ^{249}Cf(^{12}C,2α3n)].

The γ-emitting tracers used for comparison of chemical behavior were counted using a conventional NaI(Tl) crystal detector and the β-emitting isotopes with a gas-flow proportional counter.

Procedures. Solvent extraction studies on nobelium were carried out using 0.3 ml in each phase. The preequilibrated organic phase was placed in a 10 × 60 mm Pyrex tube and the product from the rabbit washed into this tube with 0.3 ml of the preequilibrated aqueous phase. Mixing was carried out using a motorized vibrating stirrer and took about 15 sec. Phase separation took an additional 15 sec. A 0.25-ml portion of each phase was then pipetted off and placed on platinum disks that sat on brass rings heated by a hot plate. Above the platinum disks were hollow rings with a number of small holes drilled at an angle such that heated helium passing through them was directed downward and inward. The heated helium substantially speeded the evaporation of the drops and the annular flow pattern kept the drops on the platinum plates centered and circular. The drying time was about 2 min for 0.25 ml of aqueous solution and somewhat shorter for the organic solvents. The same drying system was used for the column experiments. For the solvent extraction experiments the total elapsed time from end of bombardment to start of counting was about 3.5 min. The two plates from each solvent extraction equilibration were counted simultaneously for the same length of time. About 200 counts total (both phases) were accumulated for each equilibration. The distribution coefficient D_{No} was obtained from the ratio counts(org)/counts(aq). Since the accuracy of D_{m} is mostly determined by the standard deviation of the number of counts in the low phase, the experiment was repeated and collection of counts continued until a number of counts in the low phase consistent with the required accuracy of D_{No} was obtained. For example in the pH dependence experiment 10–100 counts were collected in the low phase for each experimental point.

Tracer studies involving elements for comparison used ^{7}Be, ^{27}Mg, ^{47}Ca, ^{90}Sr, ^{85}Sr, ^{133}Ba, ^{226}Ra, ^{109}Cd, ^{203}Hg, ^{67}Cu, and ^{60}Co. Solvent extraction equilibrations using these elements were done using the same 0.3-ml volume, mixing technique, and time as was used for nobelium; and, in addition, equilibrations using 5-ml volumes and longer equilibration times were done and were in excellent agreement with the small volume–short time equilibrations. Tracer only, with no carrier added, was used for the comparison elements.

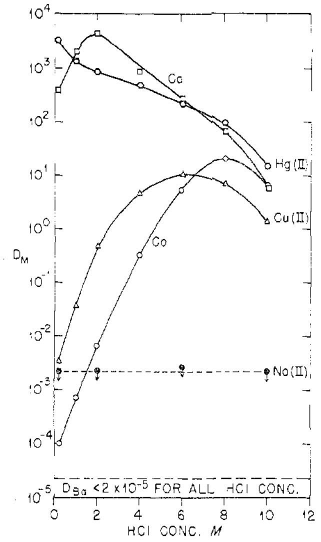

Figure 1. Comparison of No^{2+} complexing ability with Cl$^-$ ion with other divalent cations using extractability into 0.1 *M* tri-*n*-octylamine chloride in toluene from aqueous HCl.

Column experiments were carried out with bis(2-ethylhexyl)-phosphoric acid (HDEHP) adsorbed on Bio-Glass 500 (particle size 200–325 mesh).[8] The beads were treated with hexamethyldisilizane (HMDS) and loaded with 400 mg of HDEHP/g of glass. The 2 mm × 4 cm column was heated to 75° and run under pressure to attain a maximum speed (~6 drops/min) consistent with adequate resolution. The activity was loaded in ~5 drops of 0.004 *M* HCl and eluted with 0.025 *M* HCl which gave adequate separation of the peaks. ^{47}Ca and ^{90}Sr were used as internal tracers along with the ^{255}No. The total elapsed time to run a column separation was about 8 min.

The ion-exchange studies were made with Dowex 50-X12 in the acid form and having a particle size of about 10 μ. The 2 mm × 4 cm columns were run at 75° at 6 drops/min. The elution was with 4 *M* HCl. The total elapsed time for running the nobelium columns was about 10 min.

Three-drop quantities were collected on platinum disks, dried, and counted as described above to obtain the elution peak position for the Dowex 50–4 *M* HCl system, and 5 drops per plate was used for the HDEHP column.

Reagents. The tri-*n*-octylamine (TOA) was Eastman practical grade purified by scrubbing a 0.5 *M* solution in toluene with 3 or more equal volumes of water, converting the amine to the chloride form, and repeating the water scrub. This procedure removes many low molecular weight impurities. The stock solution was standardized by potentiometric titration with HClO$_4$ in dioxane after reconversion to the free amine. The 0.100 *M* solutions used in the extraction studies were made by dilution from the standardized stock and preequilibration with the HCl solution to be used in the extraction.

The HDEHP was obtained from Union Carbide Chemicals Division. As received the material contained about 1% impurities, of unknown nature, but probably 2-ethylhexanol and other alcohols. A 0.15 *M* solution in *n*-octane was converted to the sodium salt form with NaOH and scrubbed with saturated sodium sulfate. The NaDEHP solution was then reconverted to the acid form with dilute H$_2$SO$_4$ and scrubbed with distilled water. As with the amine, the 0.100 *M* solutions used in the extractions were made by dilution and preequilibrated with the aqueous phase from which extraction was to be made.

All other chemicals used were reagent grade.

Results and Discussion

In order to place nobelium chemistry in general perspective its complexing ability with chloride ion was compared with that of several divalent elements having a wide range of affinity for chloride. Figure 1 shows the extraction coefficient $D_{\mathrm{m}} = [\mathrm{M}]_{\mathrm{org}}/[\mathrm{M}]_{\mathrm{aq}}$ of Co^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, and Ba^{2+} into 0.1 *M* tri-*n*-octylamine chloride in toluene from 0.2 to

(6) C. E. Bemis, Jr., R. J. Silva, D. C. Hensley, P. F. Dittner, O. L. Keller, Jr., R. L. Hahn, J. R. Tarrant, L. D. Hunt, and C. D. Goodman, to be submitted for publication.

(7) C. E. Bemis, Jr., R. J. Silva, D. C. Hensley, O. L. Keller, Jr., J. R. Tarrant, L. D. Hunt, P. F. Dittner, R. L. Hahn, and C. D. Goodman, *Phys. Rev. Lett.*, **31**, 647 (1973).

(8) Bio-Rad Laboratories, Richmond, Calif. 94804.

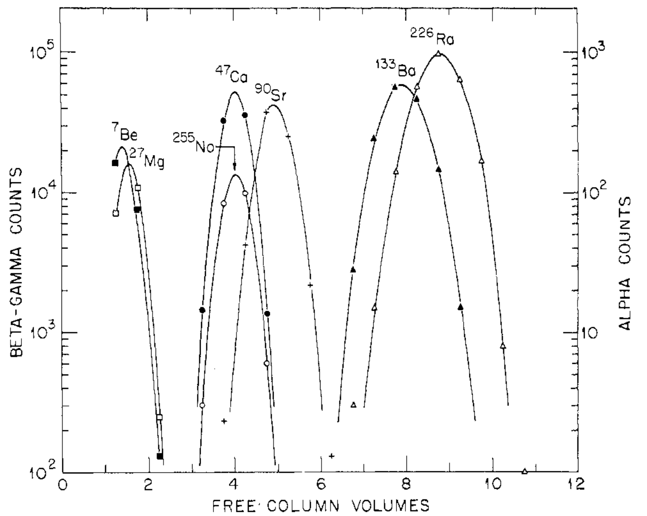

Figure 2. Comparison with alkaline earths of No^{2+} elution position from Dowex 50 with 4 *M* HCl.

10.0 *M* HCl. The elements Cd^{2+} and Hg^{2+} complex more strongly with chloride than do the other ions and thus extract most strongly into this liquid anion-exchange extractant. Co^{2+} and Cu^{2+} form moderately strong complexes and extract moderately well, better as the chloride concentration increases. For nobelium in this system we obtain 2×10^{-3} as the upper limit for the D_m at all HCl concentrations. Nobelium is therefore clearly most like the nearly noncomplexing Ba^{2+}.

Since nobelium appears most like a divalent alkaline earth in the tri-*n*-octylamine chloride extraction system, it was next compared with the alkaline earths in a Dowex 50–4 *M* HCl system. Figure 2 shows that nobelium elutes from Dowex 50 exactly at the Ca^{2+} position. Similar column elution experiments using HDEHP on an inert support *vs.* 0.025 *M* HCl showed nobelium eluting between Ca^{2+} and Sr^{2+} (Figure 3). In distribution to 0.10 *M* HDEHP in *n*-octane, nobelium also falls between Sr^{2+} and Ca^{2+} (Figure 4).

Although previous experiments,[4,5] including our own described above, pointed strongly toward nobelium being 2+ rather than 1+ in acid aqueous solutions, the possibility of its being 1+ had never actually been ruled out. Furthermore, recent work of Mikheev[9] and coworkers indicated that mendelevium can be reduced to the 1+ state. These facts prompted us to use the pH dependence of extraction by a liquid cation exchanger, bis(2-ethylhexyl)phosphoric acid (HDEHP), to verify experimentally that the nobelium ion being dealt with was indeed 2+.

It has been shown that the alkaline earths extract from nitrate systems with the second power acid dependence expected from their 2+ valence if the HDEHP cation-exchange extractant is primarily in the acid form (rather than as a salt NaDEHP or $Sr(DEHP)_2$).[10] A plot of the log D_m *vs.* pH under these conditions gives, as expected, a slope of +2 for alkaline earths Be through Ba and a slope +1 for alkalies.

For nobelium experiments the usual alkali nitrate supporting electrolyte could not be used because of the requirements of a thin source for α countings and the volatile salts tried (ammonium chloride and tetramethylammonium chloride) gave emulsion problems with HDEHP. Thus HNO_3 only was used in the aqueous phase and the pH was varied by changing its concentration. The pH dependence of Ca^{2+} and Sr^{2+} was obtained in this system (HNO_3 *vs.* 0.1 *M* HDEHP in *n*-octane) for comparison. Figure 4 shows a plot of log D_m for Sr^{2+}, Ca^{2+}, and nobelium. Calcium and nobelium show slopes of 1.9 and 2.0, respectively. (The line through the nobelium points is drawn with a slope of 2.) Strontium, however, gave an unexpected slope of 2.4 in this system. The addition of as little as 0.05 *M* $NaNO_3$ was sufficient to bring the slope down to 2.0. This behavior of strontium is not understood. It could be explained qualitatively by the formation of an inextractable nitrate complex of strontium increasing in amount in the low-pH (high-nitrate) region. Values of the formation constants reported for such a complex are not large enough to account for the deviation, however, and attempts to measure nitrate complexation by variation of nitrate concentration in the identical system used gave scattered results. In spite of this anomalous behavior of strontium, it seems certain that nobelium is clearly showing a normal 2+ valence and that the possibility of a 1+ valence under these conditions has been eliminated.

It has been shown previously that nobelium, the next to the last member of the actinide series, does not assume the 3+ oxidation state as its most stable state like its neigh-

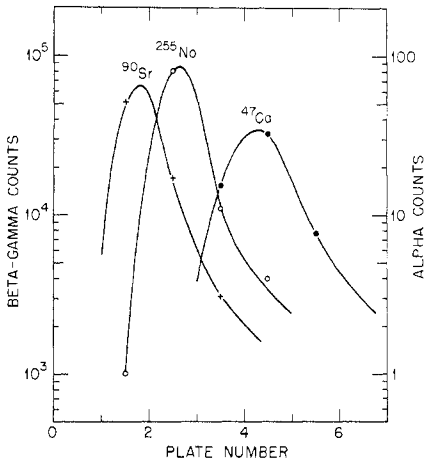

Figure 3. Elution with 0.025 *M* HCl of No^{2+} relative to Ca^{2+} and Sr^{2+} from a column using bis(2-ethylhexyl)phosphoric acid on an inert support.

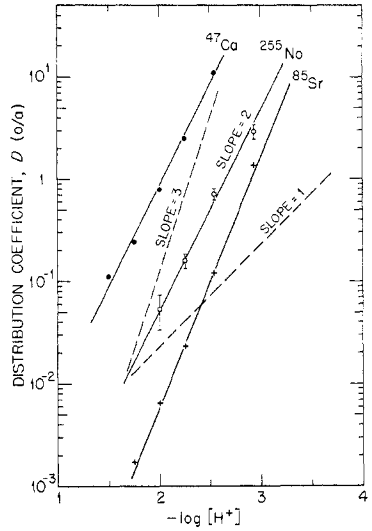

Figure 4. Distribution to 0.10 *M* bis(2-ethylhexyl)phosphoric acid in *n*-octane from aqueous HNO_3.

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(9) N. B. Mikheev, A. N. Kamenskaya, V. I. Spitsyn, I. A. Rumer, B. A. Gvozdev, and N. A. Rozenkevich, Communication 6-6341, Joint Institute of Nuclear Research, Dubna, U.S.S.R., 1972.

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Table I. Ionic Radii (Pauling)

Z	Ion	Ionic radius, Å	$r_{\max}$, Å	$\Delta(r_{\max})$,[a] Å	$\langle r \rangle$, Å	$\Delta(\langle r \rangle)$,[b] Å	Shell
4	Be^{2+}	0.31	0.14	−0.17	0.22	−0.09	$1s_{1/2}$
12	Mg^{2+}	0.65	0.25	−0.40	0.35	−0.30	$2p_{3/2}$
20	Ca^{2+}	0.99	0.54	−0.45	0.64	−0.35	$3p_{3/2}$
38	Sr^{2+}	1.13	0.68	−0.45	0.80	−0.33	$4p_{3/2}$
56	Ba^{2+}	1.35	0.87	−0.48	0.98	−0.37	$5p_{3/2}$
88	Ra^{2+}	1.40	0.97	−0.43	1.09	−0.31	$6p_{3/2}$
102	No^{2+}	1.0-1.1 (obsd) 1.1 (calcd)	0.74		0.84		$6p_{3/2}$

[a] Average $\Delta(r_{\max}) = -0.40 \pm 0.06$ Å. [b] Average $\Delta(\langle r \rangle) = -0.29 \pm 0.07$ Å.

bors.[4,5] The previous work suggests strongly, and this work confirms, that nobelium is the only one of the 28 lanthanide and actinide elements that has a 2+ valence in acid aqueous solution as its most stable state. Its counterpart in the lanthanide series, ytterbium, is most stable in the 3+ state with a reduction potential, Yb^{3+}-Yb^{2+}, of −1.15 V whereas the corresponding No^{3+}-No^{2+} couple is +1.4-1.5 V. The correlation technique of Nugent, Baybarz, Burnett, and Ryan[11] allows an understanding of the II-III redox behavior of the actinides and lanthanides in terms of the electrostatic and spin-orbit interaction energies of their f-orbital configurations as developed by Griffith,[12] Jorgensen,[13] and Vander Sluis and Nugent.[14] Our experimental and theoretical results allow, on the other hand, the first steps to an understanding of the behavior of nobelium in terms of ionic radius and fundamental thermodynamic quantities.

In Figure 5 log D_m is plotted *vs.* ionic radius for the extraction of various 2+ cations into 0.1 *M* HDEHP from aqueous solutions. The alkaline earths and Zn^{2+} and Cd^{2+} are seen to fall on a reasonably straight line. Our measured value for No^{2+} of $D_m = 0.8$ allows the estimation of its radius as 1.1 Å. The relatively noncomplexing nature of this system is indicated by the presence of Zn and Cd close to the line for the alkaline earths, but we do note that the difference in pH and salt concentration between the present and earlier work does appear to result in a difference in the log D for Ba^{2+}.

It is already known[15] that a plot of the log of the distribution coefficient *vs.* ionic radius yields a straight line for exchange of alkaline earth ions against hydrogen ions on a cation exchanger of the Dowex 50 type. This behavior suggests that our results using the Dowex 50–4 *M* HCl system can also be used to derive an ionic radius for No^{2+}. However, obtaining distribution coefficients from our ion-exchange data would be inaccurate, particularly for Be and Mg, due to an unknown interstitial and column tip volume. This error is small in the case of Ca, Sr, Ba, and Ra and for these ions a plot of log D *vs.* ionic radius gives a straight line. Based on this and on the work given by Marcus and Kertes[15] we have taken the ionic radius for No^{2+} to be the same as that of Ca^{2+} since they have exactly the same peak position in our data (Figure 2).

The empirical correlation of ionic radius with distribution coefficients of No^{2+} in these two quite different chemical systems gives essentially the same result. This agreement is clearly significant, but a theoretical analysis is highly desirable. Slater[16] and Day and Selbin[17] pointed out that the ionic radius results from the balance between the Coulomb attraction of the oppositely charged ions (in a crystal) and the repulsion arising from the overlap of the outer tails of the radial wave functions of the inert gas closed shells of the ion. Atomic theory allows the calculation of the radial position of the maximum in the electron density of the outer electronic shell (designated $r_{\max}$). This position is not appropriate for the ionic radius, however, since the outer tail alone of the wave function supplies sufficient repulsive force to counteract the Coulomb attraction of the ions. However, Slater observed that there is in many cases a constant difference between his atomic radii and Pauling's ionic radii. We show here that for the alkaline earths, at least, there is also a constant difference between $r_{\max}$ for the outermost shell of the ion and the ionic radius. In Table I we give the radius of the maximum charge density, $r_{\max}$, for the outermost electronic shell of the alkaline earth cations and No^{2+} as calculated using the Oak Ridge relativistic Hartree-Fock-Slater (rel HFS) program.[18] The radius, $\langle r \rangle$, marking the position of the average value of the charge density is also given. As shown in Table I, the differences between $r_{\max}$ and the empirical Pauling ionic radius for the alkaline earths is almost constant, $\Delta(r_{\max})$ being -0.4 ± 0.06 Å. If Be^{2+}, which has an s rather than a p outer shell, were ignored, the deviation would be even less. Similarly, $\Delta(\langle r \rangle)$ is found to

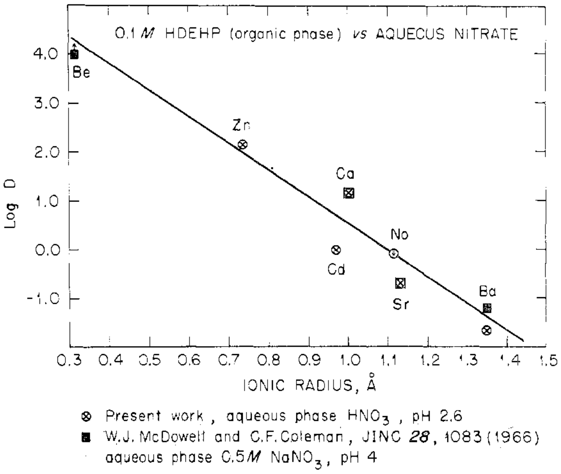

Figure 5. log D *vs.* ionic radius for typical divalent cations in the bis(2-ethylhexyl)phosphoric acid–aqueous nitrate system: ⊕, present work; aqueous phase HNO_3, pH 2.6; ■, ref 10a; aqueous phase 0.5 *M* $NaNO_3$, pH 4.

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(16) J. C. Slater, "Quantum Theory of Molecules and Solids," Vol. 2, McGraw-Hill, New York, N. Y., 1965, Chapter 4.

(17) M. C. Day, Jr., and J. Selbin, "Theoretical Inorganic Chemistry," 2nd ed, Van Nostrand-Reinhold, New York, N. Y., 1969, pp 105-117.

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be -0.29 ± 0.07 Å. The calculated $r_{\max}$ for the $6p_{3/2}$ outermost shell of No^{2+} is 0.74 Å and $\langle r \rangle$ is 0.84 Å. The No^{2+} outermost shell of $6p_{3/2}$ is the same as that of Ra^{2+} As we have shown, No^{2+} behaves chemically in a manner similar to the alkaline earths. It is therefore reasonable to suppose that the Δ's derived from the alkaline earths apply to No^{2+} as well. In this way, the ionic radius is calculated to be 1.1 Å in agreement with our results from solvent extraction and ion exchange.

As can be seen in Table I, although both No^{2+} and Ra^{2+} have the same outer shell, the radius of No^{2+} is much smaller. A similar situation is found in the comparison of Yb^{2+}, the lanthanide analog of No^{2+}, and Ba^{2+}. Beck and Barnighausen[19] give 1.03 Å as the ionic radius of Yb^{2+} for six-coordination, a value in the range of our No^{2+} value.

Our value for the ionic radius can be used to calculate the single-ion heat of hydration of the No^{2+} ion using an empirical form of the Born equation given by Phillips and Williams[20a]

$$H_{\text{hyd}} = -\frac{7.32z^2}{r + 0.85}\ \text{eV} \tag{1}$$

The value of the constant is obtained as 7.32 ± 0.08 for the alkaline earths using the values of H_{hyd} given by Phillips and Williams.[20b] This equation is found by these authors to give the single-ion hydration energies accurately for many ions including the alkali metals, the alkaline earths, Al^{3+}, Fe^{3+}, and Y^{3+}, among others. It is therefore reasonable to suppose that eq 1 will give an accurate value for No^{2+}. The value so calculated is -355 kcal $(\text{g-atom})^{-1}$ compared to -373 for Ca^{2+} and -338 for Sr^{2+}.

Acknowledgment. We wish to thank C. W. Nestor, Jr., for carrying out the rel HFS calculations, G. N. Case for assistance with the solvent extraction experiments, and Ronald C. Johnson and C. F. Baes for helpful suggestions.

Registry No. No^{2+}, 30927-24-3.

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[20] (a) C. S. G. Phillips and R. J. P. Williams, "Inorganic Chemistry," Vol. 2, Oxford University Press, London, 1966, p 58; (b) *ibid.*, Vol. 1, p 160.

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Kinetics and Mechanism of the Disproportionation of Uranium(V)

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Received March 8, 1974 AIC40162I

The kinetics and mechanism of the disproportionation of U(V) have been investigated. In agreement with a previous study (T. W. Newton and F. B. Baker, *Inorg. Chem.*, 4, 1166 (1965)), the rate of disproportionation was observed to be retarded by the presence of U(VI), the effect being attributed to the formation of a $U^V \cdot U^{VI}$ complex whose absorption spectrum in the range 360–760 nm has been measured. The effect of ionic strength, acid concentration, and the presence of complexing anions on the disproportionation rate has been examined. The reaction has also been studied in D_2O solution and reaction mechanisms are discussed.

Introduction

The kinetics and mechanism of the U(V) disproportionation reaction (eq 1) have been the subject of numerous in-

$$2UO_2^{+} + 4H^{+} \rightarrow U^{4+} + UO_2^{2+} + 2H_2O \tag{1}$$

vestigations,[1] the reaction rate usually being measured by electrochemical methods. Although there is considerable variation in the values of the reported rate constants, there has been general agreement that the reaction is second order with respect to the U(V) concentration and positive first order with respect to the acid concentration. The rate constant for the disproportionation was found[1d] to be noticeably higher in D_2O solution compared to that observed in H_2O, this observation being interpreted as indicating that the proton-transfer mechanism originally proposed by Kern and Orlemann[1a,b] was probably not applicable.

In the first study of the disproportionation using direct spectroscopic techniques, Newton and Baker[2] observed that the rate of the disproportionation decreased with increasing U(VI) concentration. This effect was attributed to the formation of a $U^V \cdot U^{VI}$ binuclear complex, and the authors were able to identify an absorption band at 737 nm as characteristic of this species. It was also shown that the value of the rate constant for the disproportionation at zero U(VI) concentration did not obey a strictly first-order acid dependency but tended to be slightly lower than expected as the acid concentration was increased.

The present study was undertaken to extend the work of Newton and Baker to higher acid concentrations, to measure the absorption spectra of U(V) and of the $U^V \cdot U^{VI}$ complex in the visible region, to reexamine the effect of deuterium substitution on the rates of disproportionation of U(V), and to determine the effect of selected anions on the reaction rate.

Experimental Section

Reagents. Solutions of $UO_2(ClO_4)_2$, $HClO_4$, $NaClO_4$, $Eu(ClO_4)_3$, and the equivalent solutions in D_2O were prepared and analyzed as described previously.[3,4] $Mg(ClO_4)_2$, which was added to the reagents in concentrations such that the sum of the UO_2^{2+} and Mg^{2+} concentration remained constant,[2] was obtained by twice recrystallizing a commercial product (Merck), the stock solution of the product being

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[3] A. Ekstrom and Y. Farrar, *Inorg. Chem.*, 11, 2610 (1972).

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