

Electromigration Method in Tracer Studies of Complex Chemistry. II. Hydrated Radii and Hydration Numbers of Trivalent Actinides

ROBERT LUNDQVIST,* E. K. HULET and P. A. BAISDEN

University of California, Lawrence Livermore Laboratory, Livermore, California 94550, U.S.A.

The hydrated radii and hydration numbers of the trivalent ions of Am, Cm, Cf, Es, Fm and Md have been derived from the measured migration velocities of these ions in an electric potential field and from Stokes' law. The migration velocities in several concentrations of aqueous perchlorate were determined and a minimum mobility, corresponding to maximum hydration, was observed for the ions of Cf and Es. We interpret our results in terms of changes in hydration, coordination number, ionic radius and ion pair formation with electrolyte composition and atomic number. Our actinide results are compared with lanthanide data.

In studying the aqueous chemistry of the actinides information about the hydration of the ions is of fundamental importance. The extent of hydration, together with the ionic charge, largely determines or influences the chemical properties of these ions. In this connection, the total hydration rather than a partial, *i.e.* the inner sphere hydration, correlates more directly with the thermodynamic properties of the ion. However, information on both inner and outer sphere hydration is, naturally, of importance.

In a previous paper in this series we discussed the general applications of the electromigration method.¹ We concluded that one of its uses is the determination of thermodynamic hydration numbers. Moreover, since this method is based on the transport properties of the ion, it may even be the most appropriate one. The electromigration method was therefore chosen for obtaining hydrated

radii and hydration numbers for the trivalent actinides.

All methods based on transport properties are potential sources of information about the extent of solvation of cations and hence diffusion or conductivity methods might also have been utilized. It was, however, believed that diffusion times would have been too long for work with short-lived nuclides like ²⁵⁶Md. Conductivity measurements could not be used because of the extremely low metal ion concentrations employed in our experiments.

EXPERIMENTAL

Procedure. The electromigration was carried out in a cellulose or glass fibre paper soaked with a perchlorate electrolyte. An electric potential of 4–12 V/cm was applied over the migration zone by the use of electrodes at the ends of the paper strip. The electrodes were separated from the paper by a electrolyte baffle system that prevented interference from the electrolysis products. The temperature was controlled by a simple thermostat which limited the temperature increase to within 1–2 °C. After each run the filter paper was dried and cut into 5 or 10 mm sections. These strips were then analyzed with an end window proportional detector for α , β and γ radiation or with a Ge(Li) crystal detector for γ . For the actinides (especially Md) the strips were treated with NH₄OH to precipitate them on the paper while the electrolyte could be washed off. Then the actinides were transferred with 6M HCl to a platinum disk giving good enough samples, after evaporation and flaming for α -spectroscopy.

A more explicit presentation of the apparatus was made in a previous paper.¹ Information about

*Department of Nuclear Chemistry, Chalmers University of Technology, S-41296 Göteborg, Sweden.

Table 1. Relative migration velocities ($Am^{3+} = 100\%$) of the trivalent actinides and Cr, Y and Eu in various perchlorate media. The electromigration measurements were performed at 7.94 V/cm at 25 °C on Whatman 41 filter paper. Under these conditions the observed migration velocities of Am^{3+} were; 1.90 mm/min (0.1 M $HClO_4$), 1.50 mm/min [1 M (0.1H,0.9Na) ClO_4], 0.40 mm/min [8 M (0.1H,7.9Na) ClO_4], 1.85 mm/min (1 M $HClO_4$) and 1.46 mm/min (1 M $NaClO_4$, pH 2–3).

Element	Radii cryst CN=6	0.1 M $HClO_4$	1 M (0.1H, 0.9Na) ClO_4	8 M (0.1H, 7.9Na) ClO_4	1 M $HClO_4$	1 M $NaClO_4$ pH 2	1 M $NaClO_4$ pH 3
^{241}Am	0.99 ⁴⁹	100	100	100	100	100	100
^{244}Cm	0.986 ⁴⁹	97 ^e	92.1	99.3	99 ^e	94.1	62.9 ^s
^{249}Cf	0.976 ⁴⁹	92.5; 90.0	89.6	96.4	96	92.6	57 ± 2 ^s
$^{253,254}Es$	0.97 ⁴⁹	90; 92	86.1; 89.4	99.1; 98.6	98	—	56 ± 2 ^s
$^{255,256}Fm$	0.96 ^e	91	93.7; 89.3	105.2; 102.6	100	—	84 ± 2
^{256}Md	0.94 ^e	93 ^e	98.8	110 ± 3	103 ^e	—	92 ± 4
^{52}Cr	0.63 ⁵⁰	93.0	91.9	—	113 ± 3	—	—
^{88}Y	0.89 ⁵⁰	—	116.3	—	—	—	—
^{152}Eu	0.950 ⁵⁰	100	98.0	110.6	97.5 ± 1.5	96.5	99.7

^e = extrapolated. ^s = possible interference from sorption.

the effects of the electrolysis on the electrolyte, choice of support material, counting techniques and viscosity measurements were also given in detail.

Nuclides and chemicals. Stock solutions of about 10⁶ dpm/ml of ^{249}Cf , ^{244}Cm and ^{253}Es in 0.1 M $HClO_4$ were prepared. ^{255}Fm ($\tau = 20$ h) was separated from its parent ^{255}Es while ^{256}Fm ($\tau = 2.6$ h) was separated from ^{256}Md by extraction chromatography. ^{256}Md was produced at the 88" cyclotron at Lawrence Berkeley Lab., Berkeley, by bombarding 0.2 μg ^{254}Es (diam. = 3 mm) on a 0.013 mm Be foil with 34 MeV helium ions. The cross-section for the (α , 2n) reaction was calculated to be 3 ± 1 mb, which includes recovering the ^{256}Md and ^{256}Fm on a Be-catcher foil (0.025 mm). Md was separated from Be by coprecipitating Md with Tb using HF. Then Fm + Tb were separated from Md by reduction of Md^{3+} to Md^{2+} with Zn(Hg) followed by extraction chromatography (HDEHP). ^{152}Eu and ^{88}Y were prepared as 0.1 M $HClO_4$ stock solutions and checked by γ -analysis to be radiochemically pure. Stock solutions of $NaClO_4$ were prepared by filtering a one-day old boiled 8 M $NaClO_4$ (p.a.) solution followed by gravimetric concentration determination. Stock solutions of conc. $HClO_4$ were standardized against NaOH. The electrolyte solutions used in the electromigration experiments were made by weighing $NaClO_4$ and $HClO_4$ stock solutions and diluting to appropriate volumes with H_2O . Other reagents were of p.a. grade and used without further purification. Hydrogen ion concentration was measured with a modified glass-calomel electrode combination as has been described previously.²

RESULTS

The observed electromigration velocity data for the trivalent actinides, Am–Md, in various perchlorate media are summarized in Table 1. The migration velocities for some other trivalent ions Cr^{3+} , γ^{3+} and Eu^{3+} were measured and the data are also reported for comparison. In all experiments Am^{3+} was run simultaneously as an internal reference. As can be seen in Table 1 the mobilities of the trivalent actinides, for a given media, are rather similar (often within 10%). Since the measured absolute migration velocity for an element may vary a few percent from different experiments (due to small variations in temperature, voltage, filter paper, density, electrolyte composition, etc.) all migration velocities were normalized by calculating the velocity relative to Am, which eliminated fluctuations in experimental conditions. Thus, the relative migration velocity could be determined to about ± 1%.

In Fig. 1 the relative mobilities of the trivalent actinides are plotted for 0.1 M $HClO_4$, 1 M $HClO_4$, 1 M (Na,H) ClO_4 at pH 1, pH 2 and pH 3 and 8 M (Na,H) ClO_4 at pH 1 as a function of the atomic number. The general picture is that the mobility decreases from Am to a minimum around Cf–Es and then increases to Md. The minimum position seems to be shifted toward Cf at high acidities or high ionic strength whereas for lower acidities or ionic strength the minimum position shifts toward Es. Further, it is indicated that the mobility of the

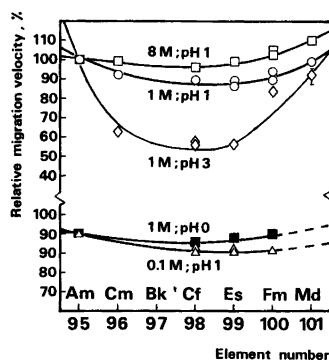


Fig. 1. Relative migration velocities of the trivalent actinides Am–Md in various perchlorate media at 25 °C. Am³⁺ mobility is used as reference (100 %). (□) denotes 8 M (0.1H,7.9Na)ClO₄, (■) 1 M HClO₄, (○) 1 M (0.1H,0.9Na)ClO₄, (△) 0.1 M HClO₄ and (◇) 1 M NaClO₄ at pH 3 (possible interference from sorption).

last element in the series, Md, has a greater mobility than Am only for the highest acidities or ionic strength. The minimum in mobility for 1 M NaClO₄ at pH 3 may be somewhat exaggerated due to possible interference from sorption.

In Fig. 5 the migration velocities are correlated with the crystal ionic radii of the elements. The migration data for the investigated trivalent ions, including Y³⁺ and Eu³⁺, in 1 M NaClO₄ at pH 4 show a minimum in migration velocity at an ionic radius of 0.97–0.98 Å. Noticeable is also that the two lanthanides fit into the graph for the trivalent actinides.

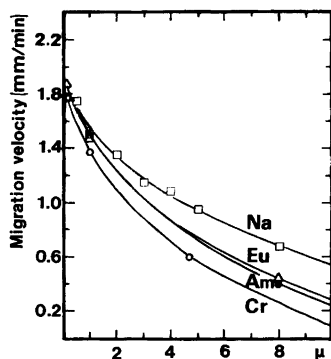


Fig. 2. Migration velocity of Am³⁺, Cr³⁺, Eu³⁺ and Na⁺ in perchlorate media as a function of the ionic strength μ , 25 °C.

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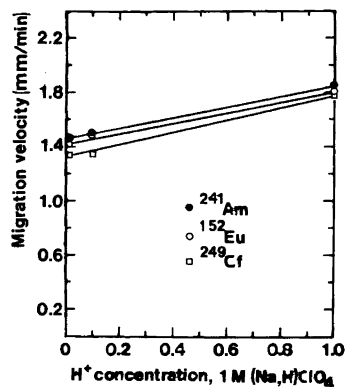


Fig. 3. Influence of acidity at constant ionic strength of the migration velocities of Am³⁺, Cr³⁺ and Eu³⁺. 1 M (Na,H)ClO₄. Whatman 41 filter paper, 7.94 V/cm and 25 °C. (●) denotes ²⁴¹Am, (□) ²⁴⁹Cf and (○) ¹⁵²Eu.

The influence of the composition of the perchlorate media on the migration was studied by varying acidity and ionic strength. Fig. 2 shows the decrease in migration of Am³⁺, Eu³⁺, Cr³⁺ and Na⁺ when increasing the ionic strength from 0.1 M to 8 M at pH = 1. The behaviour of Am³⁺ and Eu³⁺ in 0.1–8 M (Na,H)ClO₄ at pH 1 were almost the same. Eu³⁺ increased its velocity slightly relative to Am³⁺ at high ionic strengths. Cr³⁺ moved somewhat slower than Am³⁺ and Eu³⁺ while Na⁺ became the fastest ion at high ionic strength. In Fig 3 the effect of substituting Na⁺ with H⁺ at 1 M

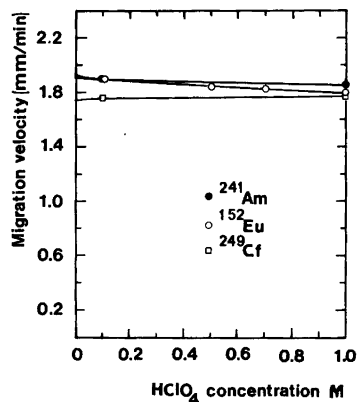


Fig. 4. Influence of perchloric acid concentration on the migration of Am³⁺, Cf³⁺ and Eu³⁺. Whatman 41 filter paper and 7.94 V/cm, 25 °C. (●) denotes ²⁴¹Am, (□) ²⁴⁹Cf and (○) ¹⁵²Eu.

ionic strength is presented showing that the migration velocity increased with increasing acidity. However, the migration velocity in dilute perchloric acid, 0.1–1 M, was nearly constant, see Fig. 4.

In order to avoid sorption phenomena a hydrogen ion concentration higher or equal to 0.001 M had to be used. Otherwise sorption (or hydrolysis) could be noted, especially for Cm, Cf and Es, by tailing of the migration band or by reduced migration velocity.

DISCUSSION

Coordination numbers. According to Stokes' law the migration velocity is inversely proportional to the effective hydrated radius of the ion. Hence, one finds, from Fig. 1, that the size of the trivalent actinides in perchlorate media slowly increases from Am to around Cf–Es and then decreases with higher atomic numbers up to Md. The unhydrated ionic radii, however, are expected to decrease monotonically from Am to Md as indicated from crystal ionic radii (Table 1). The increase in hydrated radius from Am to Cf–Es can be explained by the stronger attraction of water molecules by the smaller central ions. The reversal in this trend around Cf–Es may indicate a change in coordination number, CN.

Coordination numbers in solution are generally not known with certainty, neither for the actinides nor for the lanthanides.^{3–5} For the trivalent lanthanides CN for several solid hydrates are known. However, the coordination structure in the solid state may not be relevant for ions in solution. Although some kind of short range order must exist, it may be impossible to assign any specific geometry to the coordination of the complexed ion in solution. The use of CN may thus be improper.

With decreasing radius of the lanthanide ion from La³⁺ to Lu³⁺ the surface charge density increases. This results in an increase in total hydration energy of the ion in an aqueous solution. The ion is hydrated both in an inner and an outer sphere with the water molecules in the inner coordination sphere being rather closely packed around the metal cation. Therefore, the number of water molecules in this primary shell cannot increase with the atomic number since the space will be reduced with decreased radius. On the contrary there may be insufficient space for all water molecules resulting in a reduction in the CN. Such

a reduction is indicated by changes in the solution chemistry properties along the lanthanide series. It should, however, be emphasized that no direct proof for a reduction has been given. A change in CN may, for example, be questioned from recent X-ray solution investigations⁶ and studies of heat capacities,⁷ suggesting that the observed effects are due to changes in oxygen–metal bond distances. However, indications for a reduction in CN have been obtained from a long series of investigations of the properties of the lanthanides in solution. Measurements of conductance,^{8,9} osmotic coefficients,^{10–12} viscosities,^{13–16} heat of dilution,^{17–21} densities (molar volumes),^{22–25} specific heats^{21,26–28} and calculations of ionic entropies^{21,29} and entropies of hydration²⁰ have been made. Further support has been gained from spectroscopic measurements of relaxation frequencies,^{30–32} and hypersensitive transitions in the adsorption band.³³ Independent support has also been given by recrystallization³⁴ and by complexation studies.^{35,36} Often it was demonstrated that various thermodynamic properties are not monotone functions of the lanthanide ionic radius. The functions are S-shaped curves indicating that they consist of two series, representing the lighter and the heavier lanthanides. A transition between the two series occurs in the middle of the lanthanide series, most likely between Nd and Tb. It is thus believed that a reduction in CN from CN=9 for the heavier lanthanides to CN=8 for the lighter lanthanides to CN=8 for the lighter lanthanides occurs between Nd and Tb. For a few intermediary elements both CN may exist in equilibrium with each other.

When comparing with the obtained results for the trivalent actinides it seems that the reason for a possible change in CN is not primarily correlated with the electronic configuration changes. It is indicated that the minimum in migration velocity occurs at about the same ionic radii rather than at similar electronic configurations, Fig. 5. Furthermore, the suggested CN change for the lanthanides occurs for an ionic radius of about 0.96 Å (Pm³⁺ 0.98 Å, Gd³⁺ 0.94 Å, Table 3) which is comparable with the critical ionic radius for the trivalent actinides which is 0.97–0.98 Å (Cf³⁺ 0.98 Å, Es³⁺ 0.97 Å, Table 1), corresponding to the position of the minimum in migration velocity.

For the lanthanides there seems to be no apparent minimum in the limiting equivalent conductivity

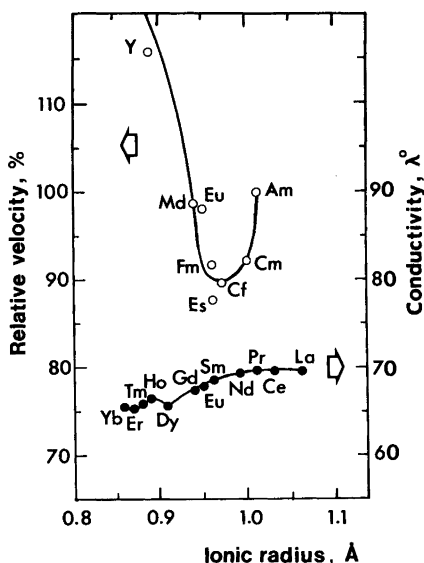


Fig. 5. The correlation of the relative migration velocity (%) of the trivalent actinides or the limiting equivalent conductance λ° for the lanthanides with the crystal ionic radii. Actinide migration velocities are relative to Am^{3+} in 1 M NaClO_4 at pH 1 and 25 °C. λ° ($\text{cm}^2 \text{ohm}^{-1} \text{equiv.}^{-1}$) for the lanthanides refers to water at 25 °C. The crystal ionic radii corresponds to 6-coordination (Tables 1 and 3). Migration velocities for Y^{3+} and Eu^{3+} are shown for comparison.

λ° in water, Fig. 5. The reason for the actinides to show a pronounced minimum in the transport properties (represented by the migration velocity) may be that different media are referred to for the lanthanides and the actinides. The λ° is calculated for zero ionic strength whereas the migration velocities are measured at 1 M ionic strength. The minimum for the actinides is anticipated to be weaker at zero ionic strength since the minimum becomes more distinct with increasing electrolyte concentration. Furthermore, chemical differences between the lanthanides and the actinides, due to greater shielding of the 4f electrons relative to the 5f electrons, may account for the less pronounced minimum in the conductivity of the lanthanides. The more effective shielding of 4f results, among other effects, in a weaker contraction of the ionic radius of the actinides than for the lanthanides.^{3,37}

Hydrated radii and hydration numbers. The obtained migration velocity data for the actinides can

be used to derive hydrated radii and hydration numbers by employing Stokes' law, eqn. (1), where

$$r = F/(6\pi\eta v) \quad (1)$$

F is the force exerted on the ion of charge ze by the electric field E giving rise to the velocity v in the hydrodynamic continuum with a viscosity of η . In a previous paper we have discussed the limitations of Stokes' law in its application to electromigration.¹ In order to use eqn. (1) one has to consider the following three aspects. Firstly, one must extrapolate the migration velocity data to infinitely dilute solutions. This has to be done to avoid the influence of complex or ion-pair formation between the cation and the electrolyte anions which would result in radii reflecting something else than the hydrated size. The extrapolation to zero ionic strength can be approximated using Jones-Doles law since the migration velocity is a linear function of the square root of the electrolyte concentration, \sqrt{c} .¹ Secondly, one must correct for the retention of the migrating ion due to the hindrance of the free migration of the ion by the paper matrix. The ratio between the observed migration velocity v_{obs} and the free migration velocity v° is defined by the obstruction factor $p = v_{\text{obs}}/v^\circ$. This factor was found to be constant for +1, +2 and +3 ions and here we have used Eu^{3+} as a reference ion to calculate the obstruction factor representative for the trivalent actinides and lanthanides. The value $p = 0.582$ is derived from the observed migration velocity of Eu^{3+} in water and the free migration velocity, as measured by its conductivity λ° in water. Eqn. (2) follows, where F is Faradays constant and N

$$\lambda^\circ = \frac{F^2}{NEe} \cdot v^\circ = \text{const.} \cdot v^\circ \quad (2)$$

Avogadros number, E the electric field and e the charge of the electron. One obtains $v^\circ = 0.494\lambda^\circ$ (mm/min at 7.94 V/cm and λ° is in $\text{cm}^2 \Omega^{-1} \text{equiv.}^{-1}$). Thirdly, one must consider that the Stokes' law radius r_s will be somewhat too small in comparison with the true hydrated radii r_h . This is the result of the imperfection of Stokes' law for ions smaller than about 5 Å.³⁸ Correction factors r_h/r_s for smaller ions in water can, however, be estimated according to Nightingale.³⁹ Except for the surface area factor 1/6 the Stokes' law is believed to be of the correct form for the trivalent lanthanides and actinides, which have sufficiently high charge

Table 2. Hydration numbers h for the trivalent actinides. Calculated from electromigration velocities v_{obs}° extrapolated to H_2O at 25°C . Stokes' law radii $r_s^{\circ} = E|z|ep/(6\pi\eta^{\circ}v_{\text{obs}}^{\circ})$, where $E = 7.94 \text{ V/cm}$, $\eta^{\circ} = 0.008903$ poise and $p = 0.582$ are corrected according to Refs. 38 and 39. The liquid volume of water is $30 \text{ \AA}^3/\text{molecule}$.

An^{3+}	$v_{\text{obs}}^{\circ} (\text{H}_2\text{O})$ mm/min ± 0.02	r_s° \AA	correction r_h°/r_s°	r_h° \AA	h $\frac{4\pi(r_h^{\circ})^3}{3 \cdot 30}$ ± 0.3
Am	1.93	4.11	1.12	4.60	13.6
Cm	1.85	4.29	1.09	4.69	14.4
Cf	1.70	4.67	1.05	4.90	16.4
Es	1.69	4.70	1.05	4.92	16.6
Fm	1.67	4.75	1.04	4.95	16.9
Md	1.71	4.64	1.05	4.88	16.2
Eu	1.95	4.07	1.13	4.58	13.4

Table 3. Hydration numbers h for the lanthanides. Calculated from λ° for water at 25°C . Stokes' law radii $r_s = 0.820|z|/\lambda^{\circ}\eta^{\circ}$ are corrected according to Refs. 38 and 39. $\eta^{\circ} = 0.008903$ poise, and the liquid volume of water molecule = 30 \AA^3 .

Ln^{3+}	Radii ⁴⁹ \AA , cryst 6-coord	$\lambda^{\circ 38}$ $\text{cm}^2 \Omega^{-1}$ equiv. ⁻¹	r_s° \AA	correction r_h°/r_s°	r_h° \AA	h $\frac{4\pi(r_h^{\circ})^3}{3 \times 30}$	h_i inner sphere	h_o outer sphere
La	1.061	69.7	3.96	1.14	4.51	12.8	9	3.8
Ce	1.034	69.8	3.96	1.14	4.51	12.8	9	3.8
Pr	1.013	69.6	3.97	1.14	4.52	12.9	9	3.9
Nd	0.995	69.4	3.98	1.14	4.53	13.0	9	4.0
Pm	(0.979)							
Sm	0.964	68.5	4.03	1.13	4.55	13.2	8.5	4.7
Eu	0.950	67.8	4.08	1.13	4.58	13.4	8.5	4.9
Gd	0.938	67.3	4.11	1.12	4.60	13.6	8.5	5.1
Tb	0.923							
Dy	0.908	65.6	4.21	1.10	4.65	14.0	8	6.0
Ho	0.894	66.3	4.17	1.11	4.62	13.8	8	5.8
Er	0.881	65.9	4.19	1.11	4.64	13.9	8	5.9
Tm	0.869	65.4	4.22	1.10	4.65	14.0	8	6.0
Yb	0.858	65.6	4.21	1.10	4.65	14.0	8	6.0
Lu	0.848							

density to form firmly hydrated entities.

The calculated hydrated radii r_h can be transformed into hydration numbers h by dividing the volume of the hydrated sphere with the liquid volume of a water molecule.* Since the volume occupied by the bare metal ion is small, 2. to 5 \AA^3 for Ln^{3+} and An^{3+} , it can be neglected in comparison with the volume of the water molecules. The obtained hydrated radii and hydration numbers for the trivalent actinides $\text{Am}^{3+} - \text{Md}^{3+}$ are given in

* The liquid volume of pure water³⁸ was used here although the volume of a water molecule in a hydrated sphere may be different.

Table 2.

For comparison, the hydration numbers for the trivalent lanthanides can be estimated in a similar way using limiting equivalent conductivity λ° data.³⁸ For this purpose Stokes' law can be written as eqn. (3).

$$\lambda^{\circ} = |z|F^2/(6\pi N\eta^{\circ}r) \quad (3)$$

The calculated h values, ranging from 12.8–14.0, are presented in Table 3. Estimates of h differ somewhat with different methods of calculation, but they consistently show an increase in h with 10–20% throughout the lanthanide series.²⁰ Hy-

dration numbers range from 9.0–11.0 and 12.8–13.9 as calculated from partial molar volumes⁴⁰ and conductivities.⁴¹ From activity coefficient data of concentrated LaCl_3 solutions a mean hydration number $h=7.5$ was derived.⁴² The hydration numbers calculated for the lanthanides in Table 3 represent the sum of the mean number of water molecules in the outer h_o and the inner h_i coordination sphere. As discussed above, the probable values of $h_i = \text{CN}$ for the lighter and the heavier lanthanides are 9 and 8, respectively. Since h simultaneously is monotonically increasing from 13 to 14 one might conclude that h_o increases from 4 to 6. For the intermediary elements, Pm–Nd, a mixture of $h_i=9$ or 8 and $h_o=4$ or 6 may exist in equilibrium with each other. An increase in h_o would be probable because the charge density increases with decreasing ionic radius.

The general trends for the trivalent actinides are more difficult to discuss since we have data only for the heavier members. Unlike the Ln^{3+} a maximum in h is found for the An^{3+} . This is an unexpected observation since the ionic radius monotonically decreases. One would be bound to assume that h should decrease monotonically. The uncertainties in the values of h are rather large because the ionic radius is used in the third power. However, the h values relative to each other within the series of actinides investigated, and in relation to Eu, may be used for a qualitative comparison. Improved values require more experiments, particularly at very low ionic strength.

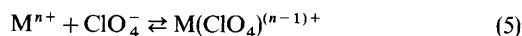
Our studies indicate that the trivalent actinides are somewhat more hydrated than the lanthanides, especially for the later members in the actinide series Cf–Md. In comparison with the lanthanides of similar ionic radius up to three more water molecules may be coordinated. This finding seems reasonable as the degree of covalency in the An^{3+} ligand bonding is probably larger since the 5f orbitals are less shielded than the 4f.^{43,44} The bonding is primarily of electrostatic nature but some interaction has been shown with the rare earth 6s or 4f orbitals.^{43,45–48} Furthermore, it has been indicated that a $\text{CN}=10$ exists for Am^{3+} complexed with aminopolyacetic acids.⁴⁴

Ion pair formation and dehydration. The reduction in migration velocities with increasing perchlorate concentration, as is shown in Fig. 2, can be interpreted in terms of ion-pair formation and dehydration. The effect of ion-pair formation is a decrease in migration velocity since the effective

charge of the ion is reduced. The opposite effect is obtained in dehydration due to the simultaneous reduction in size. In order to compare migration velocities for different ionic strengths we must also account for the changing viscosity by calculating eqn. (4), where the corrected migration velocity

$$v_{\text{corr}} = v\eta/\eta^0 \quad (4)$$

v_{corr} is the expected migration velocity at a standard viscosity (η^0). (η^0) is the viscosity of water. The initial reduction in v_{corr} , see Fig. 6, with increasing perchlorate concentration can be used to calculate the stability of the ion pair formation according to the relation (5).



The following formation constants β_1 were estimated at zero ionic strength: $\text{Am}^{3+} \approx \text{Eu}^{3+}$ ($\beta_1 = 0.6 \pm 0.1$), Cr^{3+} ($\beta_1 = 1.4 \pm 0.3$) and Na^+ ($\beta_1 = 0.20 \pm 0.05$). The results seems reasonable and the ion pair formation strength is correlated with the metal ion charge density. Furthermore the value for Am^{3+} is comparable with another estimate of $\beta_1 \approx 0.9$ obtained in a solvent extraction study.⁵¹

The migration data up to about 1 M ionic strength can be described by ion pair formation whereas the data for higher ionic strengths indicate successively

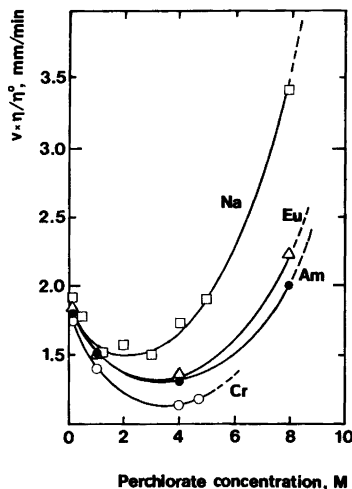


Fig. 6. Migration velocities corrected for the viscosity ($v_{\text{corr}} = v\eta/\eta^0$) of Am^{3+} , Eu^{3+} , Na^+ , and Cr^{3+} in sodium perchlorate solutions at $\text{pH}=1$ and 25°C .

stronger dehydration with increasing perchlorate concentration. Thus, almost complete dehydration is indicated, by the formal use of Stokes' law, at 8 M ionic strength. However, such complete dehydration seems unlikely. The maximum extent of dehydration is expected to be a removal of the outersphere water molecules h_o , leaving the inner sphere intact.³² This finding came from measurements of saturated lanthanide perchlorate solutions where h was found to be close to 12 and where it was concluded that ion pair formation was not strong enough to replace any of the inner coordinated H_2O with ClO_4^- . An explanation, why the migration data at 8 M $NaClO_4$ probably overestimates the dehydration, may be that Nigthingale's correction of Stokes' law is not constant but increases with electrolyte concentration. The correction accounts for the imperfections of Stokes' law and was derived at zero ionic strength. For these reasons it seems impossible to quantitatively interpret the migration velocities at higher ionic strengths.

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REFERENCES

- Lundqvist, R. *Acta Chem. Scand. A* 35 (1981) 31.
- Lundqvist, R. *Acta Chem. Scand. A* 28 (1974) 243.
- Ahrland, S., Liljenzin, J. O. and Rydberg, J. *Comprehensive Inorganic Chemistry*, Pergamon, Elmsford and Oxford 1973, Vol. 5, p. 465.
- Karraker, D. G. *J. Chem. Educ.* 47 (1970) 424.
- Jones, D. D. and Choppin, G. R. *Actinides Rev.* 3 (1969) 311.
- Grenthe, E. *Private communication*.
- Grenthe, I., Hessler, G. and Ots, H. *Acta Chem. Scand.* 27 (1973) 2543.
- Spedding, F. H., Rard, J. A. and Saeger, V. W. *J. Chem. Eng. Data* 19 (1974) 373.
- Spedding, F. H. and Rard, J. A. *J. Phys. Chem.* 78 (1974) 1435.
- Spedding, F. H., Weber, H. O., Saeger, V. W., Petheram, H. H., Rard, J. A. and Habenschuss, A. *J. Chem. Eng. Data* 21 (1976) 341.
- Rard, J. A., Weber, H. O. and Spedding, F. H. *J. Chem. Eng. Data* 22 (1977) 187.
- Rard, J. A., Shiers, L. E., Heiser, D. J. and Spedding, F. H. *J. Chem. Eng. Data* 22 (1977) 337.
- Spedding, F. H. and Pikal, M. J. *J. Phys. Chem.* 70 (1966) 2430.
- Spedding, F. H., Witte, D. L., Shiers, L. E. and Rard, J. A. *J. Chem. Eng. Data* 19 (1974) 369.
- Spedding, F. H., Shiers, L. E. and Rard, J. A. *J. Chem. Eng. Data* 20 (1975) 66.
- Spedding, F. H., Shiers, L. E. and Rard, J. A. *J. Chem. Eng. Data* 20 (1975) 88.
- Spedding, F. H., Csejka, D. A. and DeKock, C. W. *J. Phys. Chem.* 70 (1966) 2423.
- Spedding, F. H., Derer, J. L., Mohs, M. A. and Rard, J. A. *J. Chem. Eng. Data* 21 (1976) 474.
- Spedding, F. H., DeKock, C. W., Pepple, G. W. and Habenschuss, A. *J. Chem. Eng. Data* 22 (1977) 58.
- Bertha, S. L. and Choppin, G. R. *Inorg. Chem.* 8 (1969) 613.
- Hinchey, R. J. and Cobble, J. W. *Inorg. Chem.* 9 (1970) 917.
- Spedding, F. H., Pikal, M. J. and Ayers, B. O. *J. Phys. Chem.* 70 (1966) 2440.
- Spedding, F. H., Saeger, V. W., Gray, A. K., Boneau, P. K., Brown, M. A., DeKock, C. W., Baker, J. L., Shiers, L. E., Weber, H. O. and Habenschuss, A. *J. Chem. Eng. Data* 20 (1975) 72.
- Spedding, F. H., Shiers, L. E., Brown, M. A., Derer, J. L., Swanson, D. L. and Habenschuss, A. *J. Chem. Eng. Data* 20 (1975) 81.
- Spedding, F. H., Shiers, L. E., Brown, M. A., Baker, J. L., Gutierrez, L., McDowell, L. S. and Habenschuss, A. *J. Phys. Chem.* 79 (1975) 1087.
- Spedding, F. H. and Jones, K. C. *Phys. Chem.* 70 (1966) 2450.
- Spedding, F. H., Baker, J. L. and Walters, J. P. *J. Chem. Eng. Data* 20 (1975) 189.
- Spedding, F. H., Waters, J. P. and Baker, J. L. *J. Chem. Eng. Data* 20 (1975) 438.
- Spedding, F. H., Rard, J. A. and Habenschuss, A. *J. Phys. Chem.* 81 (1977) 1069.
- Geier, G. *Ber. Bunsenges. Phys. Chem.* 69 (1965) 617.
- Graffeo, A. and Bear, J. L. *J. Inorg. Nucl. Chem.* 30 (1968) 1577.
- Garnsey, R. and Ebdon, D. W. *J. Am. Chem. Soc.* 91 (1969) 50.
- Karraker, D. G. *Inorg. Chem.* 7 (1968) 473.
- Mioduski, T. and Siekierski, S. *J. Inorg. Nucl. Chem.* 37 (1975) 1647.
- Anderegg, G. and Wenk, F. *Helv. Chim. Acta* 54 (1971) 216.
- Choppin, G. R., *XIIIth Intern. Conf. Coord. Chem.*, Krakow-Zakopane 1970, p. 23.

37. Kanellakopoulos, B. *Chem. Ztg.* 97 (1973) 515.
38. Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions*, 2nd Ed., Butterworth, London 1959.
39. Nightingale, E. R. *J. Phys. Chem.* 63 (1959) 1381.
40. Padova, J. *J. Phys. Chem.* 71 (1967) 2347.
41. Choppin, G. R. and Graffeo, A. J. *Inorg. Chem.* 4 (1965) 1254.
42. Gluecklauf, E. *Trans. Faraday Soc.* 51 (1955) 1235.
43. Choppin, G. R. *XIIIth Intern. Conf. Coord. Chem.*, Krakow-Zakopane 1970, p. 23.
44. Site, A. D. and Baybarz, R. D. *J. Inorg. Nucl. Chem.* 31 (1969) 2201.
45. Nakamura, K. and Kawamura, K. *Bull. Chem. Soc. Jpn.* 44 (1971) 330.
46. Lewis, W. B., Jackson, J. A., Lemons, J. F. and Taube, H. *J. Phys. Chem.* 36 (1962) 694.
47. Rueben, J. and Fiat, D. *J. Chem. Phys.* 51 (1969) 4909 and 4918.
48. Katzin, L. I. and Barnett, M. L. *J. Phys. Chem.* 68 (1964) 3779.
49. Keller, C. *The Chemistry of the Transuranium Elements*, Verlag Chem., Weinheim/Bergst. 1971, 125.
50. Jesson, J. P. and Meutterties, E. L. *Chemist's Guide, Basic Chemical and Physical Data*, Dekker, New York 1969.
51. Baisden, P. A., Choppin, G. R. and Kinard, W. F. *J. Inorg. Nucl. Chem.* 34 (1972) 2029.

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