Ion Mobilities of Trivalent f-Elements in Aqueous Electrolytes*

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Summary

Individual ion mobilities $u_{\text{mob}}$ of carrier-free La(III), Eu(III), Gd(III), Tb(III), Tm(III), Yb(III), Lu(III), Am(III) and Cm(III) were measured in dependence on the pH of aqueous perchlorate electrolytes at $\mu = 0.10$, $T = 298.1$ K. Two different levels of ion mobilities were found in neutral (pH > 5) and acidic (pH < 2.5) solutions for most of the cations investigated. Exceptions are Eu(III) and Cm(III).

The observed relationships between the crystallographic radii of the trivalent f-elements and their $u_{\text{mob}}$, data in acidic and neutral electrolytes confirm the hypothesis of S-shaped changes of hydration parameters within the lanthanide and actinide series.

1. Introduction

Methods based on transport properties have been proven to be useful to obtain information on the physicochemical parameters of the moving ion and the interactions between the moving ion and the electrolyte system. The radiochemical methods usually applied have been the open-end capillary method to measure diffusion coefficients and electrophoresis on chromatographic materials to measure ion mobilities. For actinides and lanthanides such investigations have been carried out by Lundqvist [1] and in particular, by Fourest, David and coworkers [2—7]. A lot of interesting results on the hydration of the f-elements and correlations between the experimental data and the radii of the ions have been obtained.

However, in electrophoresis studies with electrolyte solutions, stabilized by paper or other supporting materials, some drawbacks occur, which, first, influence the reproducibility of results, and, second, cause the primary experimental results to be only relative. To eliminate these disadvantages we have developed an electromigration cell for the determination of ion mobilities of carrier-free radionuclides in electrolytes free of any supporting material. The experimental set-up is shown in the Figs. 1 and 2. The special features of its design are, first, electrolyte solutions free of any supporting materials, second, continuous removal of electrolysis products from the electrode cells, which ensures a constant electrolyte composition and guarantee pH-constancy in the electromigration tube, and, third, connection of the electromigration tube to the electrode cells via hydrodynamic resistors, thereby excluding convective flows of liquid.

Other details of the apparatus are
— the platinum electrodes,
— outlet, inlet and overflow tubes in the electrode cell,
— the thermostatic casing of the electromigration tube and the electrode cells,
— inlets for electrodes to measure the electric field strength and the temperature,
— inlet for radionuclide stock solutions, and
— a fixed radioactive mark.

This set-up for direct measurement of ion mobilities in aqueous electrolytes was applied to investigations of

— infinite ion mobility of $^{140}$La$^{3+}$ [8],
— hydrolysis reactions of $^{205,206}$Bi(III) [9], $^{239}$Np(V) [10], $^{209-211}$At(I) [11], $^{169}$Yb(III) [12], $^{241}$Am(III) [13], and $^{249}$Cf(III) [14],
— protonation of $^{131}$I$^{3-}$ [15], and
— complex formations of these and other radioelements with organic and inorganic ligands [16—20].

It is the aim of the electromigration studies described here to measure ion mobilities of carrier-free trivalent lanthanides and actinides as a function of pH of aqueous perchlorate electrolytes.

2. Experimental

Informations on performing electromigration measurements using the modified set-up were published in [10]. For illustration, Fig. 3 shows a typical example of primary on-line scanning of the migration tube by a moving NaI(Tl)-scintillation detector. The distribution of $^{241}$Am(III) zones at different times is given. From this linear time to distance correlation and after normalization to the electric field strength of $1 \text{V} \cdot \text{cm}^{-1}$ the ion mobilities were calculated. The ion mobilities obtained are absolute ones and need not be corrected by introducing any apparatus or other factors.
Fig. 1. Side view (upper part) and top view (lower part) of the electromigration set-up. 1 — electromigration tube of glass, 400 mm long, 3 mm in diameter; 2, 3 — outlets for a thermosensor and voltage-measuring electrodes and for the injection of radionuclide solution; 4 — thermostatic casing; tubes to supply water for cooling electrode chambers; 5 — platinum electrodes; 6 — electrode cells; 7 — hydrodynamic resistor (nuclepore filter); 8 — fixed radioactive mark; 9 — scanning NaI(Tl)-detector.

The electrolyte solutions of composition HClO₄/NaClO₄ were prepared from bidistilled water and analytical grade chemicals without further purification. The overall ionic strength of the electrolyte systems was constant \( \mu = 0.10 \), the temperature was \( T = 298.1(1) \) K.

To obtain a relatively narrow zone, not more than 5 \( \mu l \) of the radionuclide stock solution with a pH, overall ionic strength and chemical composition close to those of the electrolyte solution were injected into the migration tube by means of a microsyringe.

Absence of any competing effects (interactions with the surface of the migration tube or electrolysis and convective flows of the electrolyte) on the radionuclide electromigration was proven by the fact that migration velocities and half-widths of the radiolabile zone are practically constant during the 2 hours required for an electromigration experiment.

Electromigration experiments were carried out at a constant electric voltage of \( 10.00(1) \) V \( \cdot \) cm\(^{-1} \) and a temperature of 298.1(1) K.

3. Results and discussion

To illustrate typical experimental results the ion mobilities of the heavier lanthanides versus pH of the inert electrolyte are given in Fig. 4. One finds constant values of ion mobility in acidic solution with pH lower than 2.5. Then the ion mobility increases with increas-
Fig. 3. Gamma-ray scanning in a typical electromigration experiment: electromigration of $^{244}$Am$^{3+}$ in 0.10 M HClO$_4$, $T = 298.1(1)$ K; electric field strength 10.00(1) V cm$^{-1}$. One channel corresponds to 2.9 mm distance and 2.5 s period. The smaller peak (M) is the fixed radioactive mark. Additional, times of peak registrations are noted.

Fig. 4. Individual ion mobilities of the carrier-free trivalent lanthanides Gd, Tb, Tm, Yb and Lu versus pH of the aqueous inert electrolyte. Electrolytes: Na(H)ClO$_4$, $\mu = 0.10$, $T = 298.1(1)$ K.

Table 1. Individual ion mobilities $\mu_{Me^{3+}}$ of trivalent $f$-elements in acidic and neutral aqueous and differences $\Delta \mu_{Me^{3+}}$ between them. Electrolytes: Na(H)ClO$_4$, $\mu = 0.10$, $T = 298.1(1)$ K. $\mu_{Me^{3+}}$ in $10^{-9}$ cm$^2$ V$^{-1}$ s$^{-1}$.

<table>
<thead>
<tr>
<th>Me$^{3+}$</th>
<th>$\mu_{Me^{3+}}$ (pH $&lt;$ 2.5)</th>
<th>$\mu_{Me^{3+}}$ (pH $&gt;$ 5.0)</th>
<th>$\Delta \mu_{Me^{3+}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>5.59(13)</td>
<td>6.33(10)</td>
<td>11.7</td>
</tr>
<tr>
<td>Eu</td>
<td>5.12(29)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Gd</td>
<td>5.17 (6)</td>
<td>6.12 (5)</td>
<td>15.5</td>
</tr>
<tr>
<td>Tb</td>
<td>5.00 (5)</td>
<td>5.85 (5)</td>
<td>14.5</td>
</tr>
<tr>
<td>Tm</td>
<td>5.03 (7)</td>
<td>5.96 (9)</td>
<td>15.6</td>
</tr>
<tr>
<td>Yb</td>
<td>5.14 (8)</td>
<td>6.11 (5)</td>
<td>15.9</td>
</tr>
<tr>
<td>Lu</td>
<td>5.03 (6)</td>
<td>5.85 (10)</td>
<td>14.0</td>
</tr>
<tr>
<td>Am</td>
<td>5.48(15)</td>
<td>6.75(15)</td>
<td>18.8</td>
</tr>
<tr>
<td>Cf</td>
<td>5.13(16)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1 summarizes all the ion mobility data of the trivalent $f$-elements investigated. There are shown the ion mobilities at pH 1 to 2.5 and at pH 5.0 to the beginning of hydrolysis. It is necessary to emphasize again that these values are immediately measured data, valid under real electrolyte conditions and absolute in character. In the last column differences between these two levels are given in per cent.

I. Correlations of type $\mu_{Me^{3+}} = f($pH$)$

The differences are considerable, but the reasons for changes of the ion mobility of one and the same radiocation in aqueous inert electrolytes are not yet clear. There are no complex formations, redox reactions or protonisation equilibria which may have an influence on the electromigration of trivalent $f$-elements. Changes of electrolyte parameters like density,
Fig. 5. Individual ion mobility of carrier-free Eu(III) versus pH of the aqueous inert electrolyte. Electrolyte: Na(H)ClO₄, μ = 0.10, T = 298.1(1) K.

Fig. 6. Individual ion mobilities of ²⁴¹Am³⁺ versus overall ionic strength of the aqueous inert electrolyte. Electrolytes: Na(H)ClO₄, pH 3, and NaClO₄, pH 5.85, T = 298.1(1) K.

dielectric constant or others between pH 1 and 7 can be neglected as well.

Dependencies of this hitherto unknown effect on electrolyte overall ionic strength, temperature and ground electrolyte ions were studied in detail for americium(III) [13].

Fig. 6 illustrates for example, how the variation of the overall ionic strength of the perchlorate electrolyte influences the ion mobilities both in neutral and acidic solutions. As noted before, the ion mobilities in neutral solution are greater than in the corresponding acidic ones. In both systems ion mobilities increase with decreasing overall ionic strength. The experimental data can be extrapolated to infinite dilution of the electrolyte. The final ion mobility in pure water seems to be identical in both systems. Its value should be of the order of \( u_{\text{Am}^3+}^0 = +7.3(2) \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1} \). It coincides with diffusion data \( u_{\text{Am}^3+}^0 = 7.22 \) and \( 7.30 \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1} \), respectively, calculated from the corresponding values of \( D_{\text{Am}^3+}^0 \), given in [22] and [3, 4]. This confirms the correctness of the electromigration measurements. In addition, a result of \( u_{\text{Am}^3+}^0 = 6.87 \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1} \), calculated from the \( u_{\text{Am}^3+}^0 \) value, was obtained by means of electromigration measurements on paper [5].

The dependence in acidic solution may be called “normal” with respect to known diffusion and conductivity results. The dependence in neutral solution is less pronounced, however. For a first interpretation of the results shown in Fig. 4 we assume two alternative states of the hydration acting in an equilibrium

\[
\{\text{Am}^3+\}_\text{neutral} + n \text{ H}^+ \overset{\beta_n}{\rightarrow} \{\text{Am}^3+ \cdot n \text{ H}^+\}_\text{acidic} \quad (1)
\]

Using the symbols \( \{\text{Me}^{3+}\}_\text{neutral} \) and \( \{\text{Me}^{3+} \cdot n \text{ H}^+\}_\text{acidic} \) we try to describe two different types of interaction of the migrating radiocation with the ground electrolyte.

The equation was treated by computer minimization of the least squares function [21], varying the number \( n \) of the hydrogen cations. As a result, a first order in \( \text{H}^+ \) concentration and a stoichiometric stability constant of \( \lg \beta_n = 4.14(25) \) for \( ^{241}\text{Am}^{3+} \) and electrolyte parameters \( \mu = 0.10(\text{ClO}_4^-) \), 298.1 K, was calculated [13]. The results for the lanthanides are summarized in Table 2, varying the number of \( n \) in eq. (1), \( n = 1, 2, 3 \). Values of \( \beta_n^2 \) for La³⁺ are not included because the experimental data of \( u_{\text{Am}^3+}^0 \) between pH 3 and 5 are not sufficient. Good agreement between experimental values \( u_{\text{Am}^3+}^0 \) and calculated parameters of the theoretical curve \( u_{\text{Am}^3+}^0 = f(\lg[H^+]) \) was found in cases of \( n = 1 \) and \( n = 2 \) for all the lanthanides given in Fig. 4.

However, eq. (1) is not an equilibrium in a classical sense but shows phenomenologically how the changes of \( u_{\text{Am}^3+}^0 \) depend on the pH of the ground electrolyte system. Thus the interpretation of the data given in Table 2 should be given by a model similar to eq. (1). A similar set of data follows for all the heavier...
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Fig. 7. Normalized individual ion mobilities of the carrier-free lanthanides Gd, Tb, Yb and Lu versus pH of the aqueous inert electrolyte. Electrolytes: Na(H)ClO₄, μ = 0.10, T = 298.1(1) K. The curves correspond to eq. (1), calculated for n = 1 and n = 2 using mean values of-lg β^₁.

The normalized experimental data then reflect the relative change of the individual ion mobility of the trivalent lanthanides versus the pH of the inert ground electrolyte, i.e. the relative increase of ion mobilities with decreasing hydrogen concentration. To illustrate the model of eq. (1), two calculated curves with n = 1 and n = 2 based on the corresponding mean values of Δμ⁰ and β^w are shown.

For the lighter lanthanides and actinides the values Δμ⁰ and also the absolute values u₃₉ are larger, however, this effect will be treated in section II. Nevertheless, values of-lg β^w are similar for all the cations showing changes of u₃₉ as a function of pH.

An important fact is that the decrease of u₃₉ with increasing ionic strength is stronger in acidic than in neutral solutions. The specific behaviour of the electromigration of Me³⁺ in neutral solutions can be described as a "screening" of interactions of the migrating cation with the electrolyte components. Substitutions in the series X = ClO₄^-, NO₃^-, Cl⁻ or changes in the overall ionic strength in neutral solutions have only a small effect on the values of u₃₉. Unfortunately, descriptions of this type follow only phenomenological criteria. Questions about the character of the hydration sphere were not answered. It is not clear which parameters of the hydration sphere change and what are the reasons for these processes.

It is of interest that discontinuous variations of parameters of the hydration sphere (in terms of coordination numbers N and hydration numbers h, for example) are known to occur in the 4f- and 5f-series as a function of the ionic radii. A value of r₃₉ = 1.07 Å was given as a "critical" ionic radius for the changes from N = 9 to N = 8 or h = 12.7 to h = 14.1 [22]. Similar processes are known for complex formations, see Ref. [23] for example. However, there is no evidence for changes of thermodynamic data of the same cation in dependence on the pH.

Changes in the properties of the central cation or in the interaction between the migrating cation and the electrolyte components in the range of pH 3—5 have not been discussed in the literature. However, a similar electromigration behaviour of carrier-free ²³⁹Np(V) was reported. Here,-lg β^ Predictor is 3.93(2) and the difference between the individual ion mobilities of ²³⁹NpO₄^₂⁻ in acidic and neutral aqueous solutions, u = 0.10 (ClO₄^⁻), T = 298.1(1) K, is 32% [24]. Furthermore, the effect was found in the case of ⁸⁷ᵐSr²⁺ electromigration in the same electrolyte systems too, but with Δu₃₉ = 11% only [25].

So, changes of individual ion mobilities of carrier-free radionuclides in aqueous inert electrolytes seem to be not a specific property of trivalent f-elements. The second conclusion is, that f⁺-cations seem to have a stronger tendency to this interaction. This is an evidence for the participation of the oxygen atoms within the f-cations with respect to this process.

To study the nature of the electromigration effect described, further investigations are necessary. In particular, ion-solvent interactions should be considered in detail. Possibly, the existence of a special level of the hydrogen bonds produces changes in the hydration character of the cation.

II. Correlations of type u₃₉ = f(r_c)

As a second aspect one can discuss the absolute values of ion mobility of other trivalent f-elements. An S-shaped curve is obtained when the data are plotted versus the crystallographic radii of the ions, Fig. 8. This correlation was discussed in detail by David, Fourest and co-workers [2—7]. The discontinuous variation of transport properties according to changes of the hydration sphere is now confirmed by directly measured ion mobilities in real electrolytes.

The lightest elements of both the lanthanide and actinide series migrate faster than the heaviest members. The change in the middle of the series results from a significant change of hydration parameters. For infinite dilution for example, one can expect changes from 9 to 8 water molecules. Dealing with ion mobilities at real electrolyte conditions it is difficult to give exact values for the parameters of the hydration sphere. However, the S-shaped curve clearly indicates changes to occur around europium for the lanthanides and around californium for the actinides.

Differences of the S-shaped curves between the 4f and 5f group will not be treated here.

The results agree with discussions of David et al. published recently [5, 7]. On the other hand, it is a new result that this behaviour occurs similarly in real acidic...
and neutral aqueous electrolytes but with different absolute values.

4. Conclusions

Finally, some conclusions should be summarized.

1. The ion mobilities, measured by means of our analytical method, are absolute ones even in real electrolytes and agree to diffusion and conductivity data obtained by other authors.

2. Electromigration measurements of some carrier-free trivalent lanthanides and actinides revealed two different plateaus of ion mobilities in acidic and neutral solutions. As the overall ionic strength decreases, the differences of the ion mobilities between acidic and neutral solutions decreases too. In an infinitely diluted solution they seem to be identical.

The effect is induced by a change in hydrogen concentration. Because of this fact two different situations in the interaction of the migrating radiocation with the electrolyte and/or water-hydrogen bond structures are proposed. Similar to known definitions of “stick” and “slip” with respect to ion migration the effect may be described as a “sensibility” of the migrating ion and its interactions with the electrolyte system in acidic solution and by a “screening” with respect to the interactions in neutral ones.

The process can be simulated phenomenologically by eq. (1). The number \( n \) of the hydrogen cations acting in this equilibrium is probably 1 or 2, the equilibrium constants for \( \text{Me}^{3+} \) are \( \log \beta_n^+ = 3.5(3) \) or \( \log \beta_2^+ = 6.9(4) \), respectively, \( \mu = 0.10 \) \((\text{ClO}_4^-) \). \( T = 298.1(1) \) K. However, a quantitative interpretation of the detected behaviour is still missing.

3. Ion mobilities of trivalent \( f \)-elements already in real electrolytes vary according to their crystallographic radii in an S-shaped curve. The critical radius for a change of hydration parameters is found for europium and californium, respectively. It should be noted, that there is a coincidence between this fact and the fact, that these elements show no dependence of ion mobility on pH.

4. Last not least it can be stated, that the modified set-up for electromigration measurements offers some interesting possibilities to study properties of ions in aqueous solution.

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References