

ELECTROMIGRATION OF CARRIER-FREE RADIONUCLIDES

IV. OXALATE AND TARTRATE COMPLEXES OF La(III) IN AQUEOUS SOLUTION

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(Received October 23, 1986)

Dependences of La(III) overall ion mobilities \bar{u} on concentrations of ox^{2-} and tart^{2-} anions of oxalic and tartaric acid in aqueous solutions of 0.01 overall ionic strength and temperature 298.1 K were obtained by direct measurements of electromigration of carrier-free ^{140}La -lanthanum(III). Concentration stability constants K_n and individual ion mobilities u_i^0 of oxalate and tartrate complexes of La(III) have been calculated for nitrate and perchlorate electrolytes, respectively:

$$[\text{La}(\text{ox})]^+, \lg K_1 = 5.63(9), \quad u^0[\text{La}(\text{ox})]^+ = +1.95(15) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1};$$

$$[\text{La}(\text{ox})_2]^{-}, \lg K_2 = 4.05(19), \quad u^0[\text{La}(\text{ox})_2]^{-} = -1.76(20) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1};$$

$$[\text{La}(\text{tart})]^+, \lg K_1 = 4.40(5), \quad u^0[\text{La}(\text{tart})]^+ = +1.99(18) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}.$$

Results are compared with literature data. Additional, limiting individual La^{3+} ion mobility was calculated: $u_{\text{La}^{3+}}^{(\mu=0)} = +6.9(1) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ for pure water at 298.1 K.

Introduction

Electrophoresis of ions in aqueous solutions is an effective analytical method for investigations of equilibrium processes like hydrolysis, complex formation, oxidation-reduction reactions.¹⁻³ For these purposes we have developed a new technique of low-voltage zone electrophoresis in aqueous electrolyte systems. The technique, described in References 4–7 in detail, allows direct measurements of migration mobilities of radionuclides. Compared to other types of electromigration technique its main feature is that ion mobilities are measured in solutions free of finely divided fillers or other supporting materials, usually employed for suppression of convective flows of liquid in the electromigration tube. In our case hydrodynamic resistors made of nuclepore filters with holes 0.03 μm in diameter were applied. The resistors closed the electromigration tube on both sides.⁷ Consequently, measured ion mobilities

are functions of only physical and chemical interactions between migrating species and properties of the background electrolyte.

First experiments on checking the applicability of the new electromigration technique for investigation of hydrolysis and complex formation of metal ions were carried out with bismuth(III) and ytterbium(III) radionuclides.⁸⁻¹⁰ Individual mobilities of ions, building up the equilibrium system, constants of hydrolysis and complex formation with anions of some dicarboxylic acids were determined. Constants of bismuth(III) hydrolysis and stability constants of oxalate and tartrate complexes of ytterbium(III) are in good agreement with literature data.^{11-13,19,22}

We found it necessary, nevertheless, to continue the series of electromigration experiments with trivalent metal cations, using La(III) for investigations. Stability constants for lanthanum(III) complexes with oxalate and tartrate ligand were determined many times by different analytical methods,¹⁴⁻²¹ and yielded more information for comparison and estimation of our results.

This paper is aimed at measuring the overall lanthanum(III) mobilities \bar{u} in aqueous electrolyte solutions of oxalate and tartrate ligands and obtaining stability constants as well as individual ion mobilities of $[LaL_n]^{3-2n}$ ions, acting in the equilibrium systems. Values obtained in the mathematical processing of the electromigration data were compared with the literature data.

Experimental

The work was done with ¹⁴⁰La radionuclide (40.3 h) generated by carrier-free ¹⁴⁰Ba placed on cation-exchange resin DOWEX 50 X 8. Radiobarium was purchased from "Isotope", Moscow. Lanthanum was separated from barium via elution by 0.5 m solution of ammonium α -oxyisobutyrate. After removing the α -OIB, a stock solution of carrier-free ¹⁴⁰La-La(III) in 0.01 m HNO₃ of about 5 GBq · ml⁻¹ specific volume activity was used for the experiments.

Lanthanum(III) electromigration was measured in solutions of the following composition:

- (1) H(K)NO₃/K₂C₂O₄;
- (2) H(K)ClO₄/K₂C₄H₄O₆;
- (3) HNO₃, $7 \cdot 10^{-4} - 2.5 \cdot 10^{-1}$ mol · l⁻¹;
- (4) HClO₄, $9 \cdot 10^{-4} - 4.3 \cdot 10^{-2}$ mol · l⁻¹;
- (5) H(K)NO₃;
- (6) H(K)ClO₄.

Electrolyte systems (1), (2), (5) and (6) were of constant overall ionic strength $\mu = 0.01$ and of $2 < \text{pH} < 3.5$. All experiments were carried out at $T = 298.1$ K.

Solutions were prepared using bidistilled water and chemically pure agents. Concentrations of oxalate and tartrate ions $[L^{2-}]$ were calculated on the basis of corresponding concentration constants of oxalic and tartaric acid dissociation.^{2,23}

Experimental procedure and details of the electromigration technique are described in previous papers.⁷⁻¹⁰

Results

When analyzing experimental data, we supposed that formation of lanthanum(III) complexes with protonated dicarboxylic ligands HL^- is much less probable than with the L^{2-} ligands under our conditions, and that effects of La(III) hydrolysis can be excluded in solutions with $pH < 3.5$. The first supposition was based on the results of our previous paper,¹⁰ where it was shown that ytterbium(III) overall ion mobility in the $2 < pH < 5.5$ interval predominantly depends on the L^{2-} concentration. The second supposition is proved by constant ion mobilities of La^{3+} at $2 < pH < 3.5$ with $+5.65(10) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ in nitrate and $+6.15(10) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ in perchlorate solutions, electrolyte systems (5) and (6), respectively.

Thus the electromigration of La(III) in oxalate and tartrate solutions is only determined by Reaction (1)



According to the migration equation

$$\bar{u}_{La(III)} = \sum_{n=0}^2 u_{[LaL_n]^{3-2n}}^0 \cdot \alpha_{[LaL_n]^{3-2n}} \quad (2)$$

the overall ion mobility of lanthanum(III) ($\bar{u}_{La(III)}$) is determined by individual ion mobilities of ions, building up the equilibrium systems ($u_{[LaL_n]^{3-2n}}^0$) and their particular mole fraction (α). For Reaction (1) with $n = 1, 2$ Eq. (2) is as follows:

$$\bar{u}_{La(III)} = \frac{u_{La^{3+}}^0 + u_{LaL^+}^0 + K_1[L^{2-}] + u_{LaL_2}^0 \cdot K_1 K_2 [L^{2-}]^2}{1 + K_1[L^{2-}] + K_1 K_2 [L^{2-}]^2} \quad (3)$$

where K_1 and K_2 are the individual concentration constants of the La(III) complexes; $\beta_2 = K_1 K_2$.

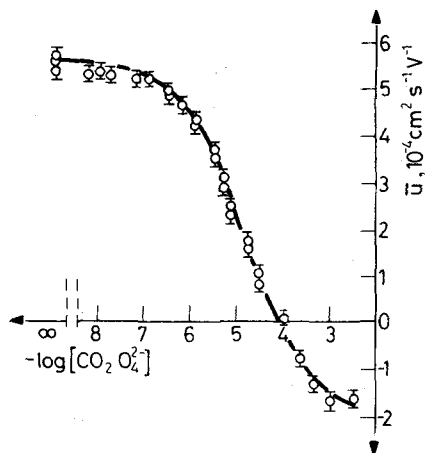


Fig. 1. ^{140}La – lanthanum(III) ion mobility vs. oxalate concentration in $\text{H}(\text{K})\text{NO}_3/\text{K}_2\text{C}_2\text{O}_4$ electrolytes; $\mu = 0.01$, $T = 298.1\text{ K}$

Table 1
Values of stoichiometric stability constants and individual ion mobilities of oxalate and tartrate complexes of $\text{La}(\text{III})$, $\mu = 0.01$, $T = 298.1\text{ (1) K}$

Electrolyte system	Ion	u_i^0 $\times 10^{-4}\text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$	$\log K_n$, (K_n in $\text{l} \cdot \text{mole}^{-1}$)
$\text{H}(\text{K})\text{NO}_3/K_2\text{C}_2\text{O}_4$ $2 < \text{pH} < 3.5$	La^{3+}	+5.65(10)	—
	LaL^+	+1.95(15)	5.63(9)
	LaL_2^-	-1.76(20)	4.05(19)
$\text{H}(\text{K})\text{ClO}_4/\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ $2.8 < \text{pH} < 3.5$	La^{3+}	+6.15(10)	—
	LaL^+	+1.99(18)	4.42(5)

Oxalate complexes of La(III)

The overall ion mobility of $\text{La}(\text{III})$ is shown in Fig. 1 as a function of the $\text{C}_2\text{O}_4^{2-}$ concentration in electrolyte (1) solutions. Both positive and negative overall ion mobilities of $\text{La}(\text{III})$ were observed. To calculate individual ion mobilities and stability constants of the mono- and dioxalate complexes, the mathematical processing of the experimental dependence $\bar{u}_{\text{La}(\text{III})} = f([\text{L}^{2-}])$ was performed by the least squares method using MINUIT program²⁴ according to Eq. (3). The calculated values of individual ion mobilities u_i^0 and stability constants K_n are listed in Table 1.

Tartrate complexes of La(III)

Figure 2 shows the overall ion mobility of La(III) as a function of the $C_4H_4O_6^{2-}$ concentration in electrolyte (2) solutions. In the whole interval of tartrate concentrations the La(III) overall mobility is positive, which was not the case in the corresponding oxalate systems.

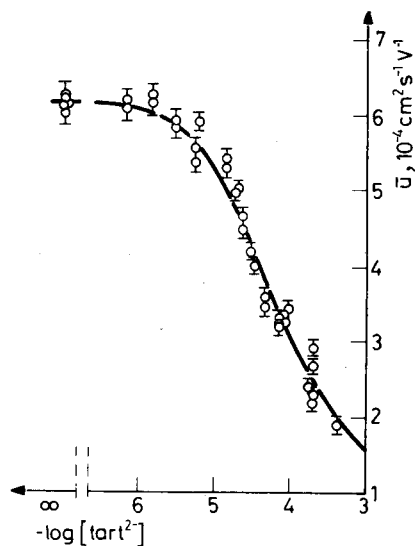


Fig. 2. ^{140}La - lanthanum(III) ion mobility vs. tartrate concentration in $\text{H}(\text{K})\text{ClO}_4/\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ electrolytes; $\mu = 0.01$, $T = 298.1 \text{ K}$

The experimental electromigration data were mathematically processed by the same mechanism as in the previous case. For the individual ion mobility of the anionic complex a value of $u_{[La(tart)_2]^-}^0 = -2.0(1.0) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ was taken in Eq. (3). Choosing this value, we assumed that values of individual ion mobilities of oxalate and tartrate complexes of La(III) are approximately the same. The parameters obtained for the La(III) tartrato complex are listed in Table 1.

Functions $\bar{u}_{La(III)} = f(K_1; K_2; u_{[LaL_n]^{3-2n}}^0; [L^{2-}])$ calculated for electrolytes (1) and (2) (lines in Fig. 1 and 2) are in good agreement with experimental points.

Individual ion mobilities

An interesting result is the difference in individual ion mobility data of La^{3+} in perchlorate and nitrate solutions: $u_{La^{3+}}^0 = +6.15(10) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ in

perchlorate solution, $u_{La^{3+}}^0 = + 5.65(10) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ in nitrate solution, respectively. This difference was observed both in direct measurements in $\mu = 0.01$ electrolyte solutions (5) and (6) without oxalate and tartrate ligands and in mathematical processing of experimental $\bar{u}_{La(III)}$ dependences on ligand concentrations in $\mu = 0.01$ electrolytes (1) and (2).

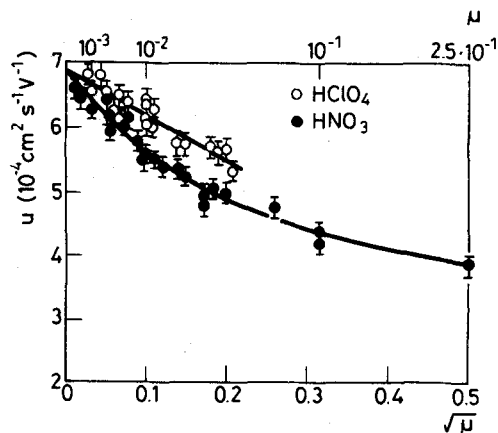


Fig. 3. $^{140}\text{La}-\text{La}^{3+}$ individual ion mobility vs. overall ionic strength of HNO_3 and HClO_4 electrolytes; $T = 298.1 \text{ K}$. Lines are filled according to JONES-DOLE equation

To obtain additional data on the influence of chemical composition of the “inert” electrolyte on La(III) ion mobilities, we have studied the electromigration of lanthanum(III) in HNO_3 and HClO_4 solutions of various concentration, i.e. various overall ionic strength. The results are shown in Fig. 3. Using those results, the limiting La^{3+} ion mobility ($u_{La^{3+}}^{\mu=0}$) in pure waters at 298.1 K can be calculated by a least squares method according to the JONES-DOLE equation:^{2,7}

$$u_{La^{3+}}^{\mu} = u_{La^{3+}}^{\mu=0} - \frac{A\sqrt{\mu}}{1 + N\sqrt{\mu}} - B \cdot \mu \quad (4)$$

The calculations with MINUIT program yielded similar values of $u_{La^{3+}}^{\mu=0}$ for both electrolyte systems: $+6.85(7) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ (HClO_4) and $+6.92(10) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ (HNO_3).

Discussion

Electromigration experiments and mathematical processing of electromigration data allowed to obtain values of individual concentration constants for oxalate and tartrate complexes of carrier-free lanthanum(III). To be compared with values, given in the literature, they should be extrapolated to zero overall ionic strength. DAVIES' empirical formula^{2,5,26}

$$\lg K_n = \lg K_n^0 + \Delta z^2 A \left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.2\mu \right) \quad (5)$$

was employed, where K_n are the individual thermodynamic stability constants,

$$\Delta z^2 = \Sigma Z^2 (\text{products}) - \Sigma Z^2 (\text{reactants}),$$

where Z – charge of ion,

A – DEBYE-HÜCKEL constant (0.511 at 298.1 K water solutions).

Thermodynamic constants obtained by this extrapolation are given in Table 2. They are in good agreement with thermodynamic stability constants of the complexes, determined by other methods. This coincidence proves acceptability of the special electromigration technique.

Table 2
Thermodynamic stability constants of oxalate
and tartrate complexes of La(III), T = 298.1 K

Ligand	Method	$\log K_1^0$	$\log K_2^0$	Reference
$C_2O_4^{2-}$	distr.	6.1(2)	4.2	14
	distr.	6.4	4.2	15
	sol.	7.4	–	16
	electromigration, amperometry,	6.1(1)	3.6	17
	electromigration,	6.2(1)	–	18
		6.2(1)	4.2(2)	present paper
$C_4H_4O_6^{2-}$	gl. el.	4.5	–	19
	gl. el.	4.6	2.99	20
	gl. el.	5.0	3.5	21
	gl. el.	4.77	–	22
	electromigration	4.9(1)	–	present paper

distr. – distribution between two phases,
sol. – solution of lanthanum oxalate,
gl. el. – measurements with a glass electrode.

Table 3
Correlations between individual ion mobilities $u_{[LaL_n]^{3-2n}}^0$ and charges $z_{[LaL_n]^{3-2n}}$ of La(III) complex ions in oxalate and tartrate electrolytes; $u = 0.01$, $T = 298.1$ K

L^{2-}	$\frac{u_{La^{3+}}^0}{u_{LaL^+}^0} \cdot \frac{z_{LaL^+}}{z_{La^{3+}}}$	$\frac{u_{La^{3+}}^0}{u_{LaL_2^-}^0} \cdot \frac{z_{LaL_2^-}}{z_{La^{3+}}}$	$\frac{u_{LaL^+}^0}{u_{LaL_2^-}^0} \cdot \frac{z_{LaL_2^-}}{z_{LaL^+}}$
	$C_2O_4^{2-}$	0.97(9)	1.07(14)
$C_4H_4O_6^{2-}$	1.03(11)	—	—

It was demonstrated that this type of electromigration measurements is suitable for investigations of equilibrium processes of carrier-free radionuclides and for determination of individual ion mobilities of separate ions in the equilibrium system. The latter is of special interest since it seems impossible to solve this problem by other methods.

Absolute individual ion mobilities of oxalate and tartrate complex ions $[LaL]^+$ and $[LaL_2]^-$ are approximately the same and almost 3 times lower than the individual La^{3+} mobility (Table 3). This is more proof of an earlier conclusion^{9,10} that the individual ion mobilities of complex ions of one and the same metal cation with organic ligands mainly depend on the charge of the complex ions.

The limiting individual ion mobility of La^{3+} cation, calculated on the basis of electromigration data in $HClO_4$ and HNO_3 of $u_{La^{3+}}^{\mu=0} = +6.9 \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ in pure water at 298.1 K appeared to be less than the one determined earlier by conductivity measurements.^{28,29} $+7.2 (1) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$. However, it coincided with the lowest published value of $+6.86 (5) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$, where effects of La(III) hydrolysis and carbonate complex formation have been taken into account.³⁰

Finally this result should be a good illustration of opportunities opened by one technique of direct measurement of ion mobilities of radionuclides in aqueous electrolyte systems.

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