

Electroosmotic effects in the determination of ion mobilities of carrier-free radionuclides in free aqueous electrolyte solutions

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Summary. A device for on-line electromigration studies of radio-elements in free electrolytes has been tested by measuring the absolute individual ion mobilities of no-carrier-added single charged anions [^{99m}Tc]TcO₄⁻ and [¹⁸F]F⁻ and differently charged cations [¹³⁷Cs]Cs⁺, [⁵⁷Co]Co²⁺ and [²⁴¹Am]Am³⁺ in inert aqueous electrolytes at 298.1 K. The observed ion mobilities were found to be influenced by electroosmosis in the migration tube. A relation to correct this effect is proposed. In addition, it was shown that the effect of electroosmosis may be suppressed by chemical treatment of the surface of the migration tube.

Introduction

In a previous article [1] we reported on the development and evaluation of an electromigration device composed of a migration cell, a γ -ray scanning unit and a data processing system, for the on-line determination of absolute individual ion mobilities of radioactive species in electrolyte systems free of any supporting material. High reproducibility rates and accuracies better than 0.5% of the migration velocities were obtained.

However, the determined absolute individual ion mobilities were found to be affected by electroosmosis under the experimental design of the glass electromigration tube of 3 mm inner diameter applied. Electroosmosis influences the migration of the ions in particular when the glass surface of the migration tube was untreated. A semi empirical expression needs to be introduced to correct this effect in order to obtain absolute migration data from the primary measured experimental values. There is, however, the possibility to suppress electroosmotic effects by chemical surface modification of the migration tube with trimethylchlorosilane or polyacrylamide. As a proof of the concept, the values of the absolute individual ion mobilities at infinite dilution were determined for the single charged anions [^{99m}Tc]TcO₄⁻ and [¹⁸F]F⁻ and the differently charged cations [¹³⁷Cs]Cs⁺, [⁵⁷Co]Co²⁺ and [²⁴¹Am]Am³⁺.

Theory

According to Onsager theory based on the Debye–Hueckel treatment of the ion atmosphere in dilute solutions [2] and to corrections proposed by Stokes *et al.* [3] for finite ion-size effects in connection with dielectric saturation and local hydration of the ions [4], the absolute individual ion mobility of an ion present at very low concentration may be given by the extended limiting law:

$$u = u^\circ - \frac{2.802 \times 10^6 z^2 u^\circ (1 - \sqrt{d(\omega)})}{(\epsilon T)^{3/2}} \times \frac{\sqrt{\mu}}{(1 + \kappa a)(1 + \kappa a/\sqrt{2})}, \quad (1)$$

where u° is the limiting (at infinite dilution) ion mobility of the ion, z the charge of the ion, ϵ the dielectric constant of the solvent, T the absolute temperature, $d(\omega)$ a mobility function, $\kappa = \sqrt{\mu}/3.041 \times 10^{-8}$ [5] the reciprocal radius of the ion atmosphere, a the closest distance of approach between ions of opposite charge and μ the overall ionic strength of the electrolyte. For NaCl and NaClO₄ electrolytes the value of a is 3.97 Å and 4.04 Å [6]. When only three kinds of ions are involved in the migration process, $d(\omega)$ is given by:

$$d(\omega) = \frac{|z|}{|z_+| + |z_-|} \left[\frac{|z_+| u_+^\circ}{|z| u_+^\circ + |z_+| u^\circ} + \frac{|z_-| u_-^\circ}{|z| u_-^\circ + |z_-| u^\circ} \right], \quad (2)$$

where z_+ and z_- are the charges of the cations and anions of the supporting electrolyte and u_+° and u_-° their limiting mobilities. The values used for the calculation of the ion mobilities at 298.1 K of the ions studied, i.e. TcO₄⁻, F⁻, Cs⁺, Co²⁺ and Am³⁺ are listed in Table 1. Substitutions of these parameters in relation (1) leads to the following expressions:

$$u_{\text{Cs}^+}/10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1} = 8.00 - \frac{2.158\sqrt{\mu}}{(1 + 1.328\sqrt{\mu})(1 + 0.939\sqrt{\mu})} \quad \text{in NaClO}_4 \quad (3)$$

$$u_{\text{Co}^{2+}}/10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1} = 5.70 - \frac{3.148\sqrt{\mu}}{(1 + 1.328\sqrt{\mu})(1 + 0.939\sqrt{\mu})} \quad \text{in NaClO}_4 \quad (4)$$

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$$u_{\text{Am}^{3+}}/10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1} = \frac{7.30 - \frac{8.05\sqrt{\mu}}{(1 + 1.328\sqrt{\mu})(1 + 0.939\sqrt{\mu})}}{\quad} \text{ in NaClO}_4 \quad (5)$$

$$u_{\text{F}^-}/10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1} = \frac{5.74 - \frac{1.277\sqrt{\mu}}{(1 + 1.328\sqrt{\mu})(1 + 0.939\sqrt{\mu})}}{\quad} \text{ in NaClO}_4 \quad (6)$$

$$u_{\text{TcO}_4^-}/10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1} = \frac{5.75 - \frac{1.232\sqrt{\mu}}{(1 + 1.305\sqrt{\mu})(1 + 0.923\sqrt{\mu})}}{\quad} \text{ in NaCl} \quad (7)$$

Table 1. Parameters used for the calculation of the theoretical ion mobilities. u° , u_+° , u_-° in $10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$; $d(\omega)$ mobility function from relation (2); $\epsilon_{\text{H}_2\text{O}}(298.1 \text{ K}) = 78.54$.

Parameters	Cs ⁺ in NaClO ₄	Co ²⁺ in NaClO ₄	Am ³⁺ in NaClO ₄	F ⁻ in NaClO ₄	TcO ₄ ⁻ in NaCl
u°	8.00 ^a	5.70 ^a	7.30 ^b	5.74 ^a	5.75 ^c
Electrolyte					
u_+°	5.19 ^a	5.19 ^a	5.19 ^a	5.19 ^a	5.19 ^a
u_-°	6.97 ^a	6.97 ^a	6.97 ^a	6.97 ^a	7.91 ^a
$d(\omega)$	0.429	0.768	0.711	0.512	0.527

a: [15]; b: [9]; c: [13].

The ion mobilities calculated with the above expressions are shown graphically for the Cs⁺, Co²⁺, Am³⁺, F⁻, and TcO₄⁻ ions in Figs. 1–5.

Experimental

Apparatus

The apparatus used in this work as well as the analytical procedure for the on-line determination of the migration velocities of radio-ions are described in detail elsewhere [1]. A bolus of 1–5 μl of the solution containing the radioisotope under investigation was injected into the migration tube

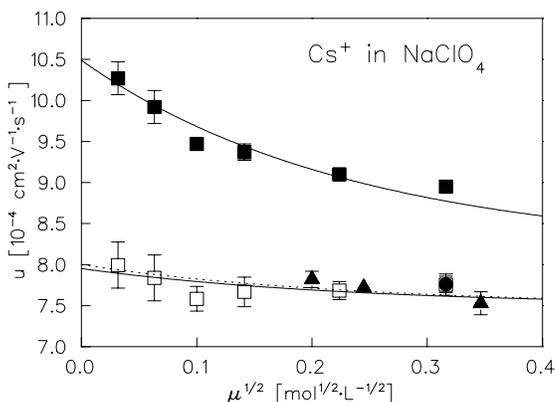


Fig. 1. Individual ion mobility of [¹³⁷Cs]Cs⁺ at different ionic strength values in aqueous NaClO₄ solutions, at 298.1 K, for a migration tube with an inner diameter of 3 mm. Experimental data with the untreated tube (close squares); data corrected for electroosmosis (open squares); experimental data with the tube coated with polyacrylamide, (close triangles), coated with TMCS (close circle); extended limiting law (dotted line).

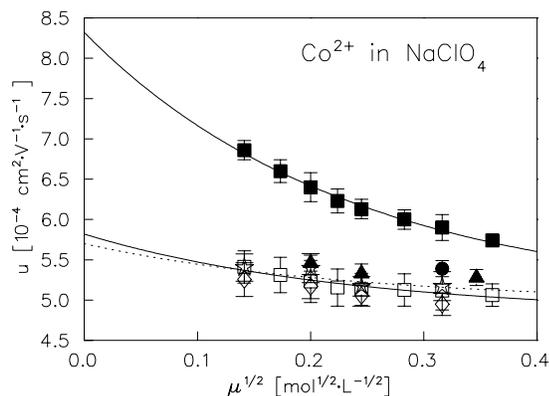


Fig. 2. Individual ion mobility of [⁵⁷Co]Co²⁺ at different ionic strength values in aqueous NaClO₄ solutions, at 298.1 K, for migration tubes with various inner diameter ϕ . Experimental data with the untreated tube, $\phi = 3 \text{ mm}$ (close squares); data corrected for electroosmosis $\phi = 3 \text{ mm}$ (open squares), $\phi = 4 \text{ mm}$ (open diamonds), $\phi = 5 \text{ mm}$ (open stars); experimental data with the tube, $\phi = 3 \text{ mm}$, coated with polyacrylamide (close triangles), coated with TMCS (close circle); extended limiting law (dotted line).

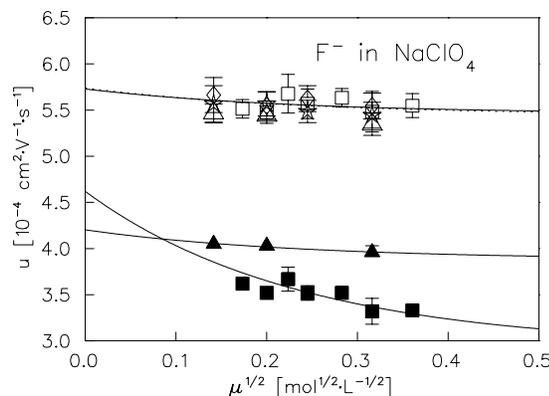


Fig. 3. Individual ion mobility of [¹⁸F]F⁻ at different ionic strength values in aqueous NaClO₄ solutions, at 298.1 K, for migration tubes with various inner diameter ϕ . Experimental data with the untreated tube, $\phi = 3 \text{ mm}$ (close squares); data corrected for electroosmosis $\phi = 3 \text{ mm}$ (open squares), $\phi = 4 \text{ mm}$ (open diamonds), $\phi = 5 \text{ mm}$ (open stars); experimental data with the tube, $\phi = 3 \text{ mm}$, coated with polyacrylamide (close triangles); data corrected for adsorption (open triangles); extended limiting law (dotted line).

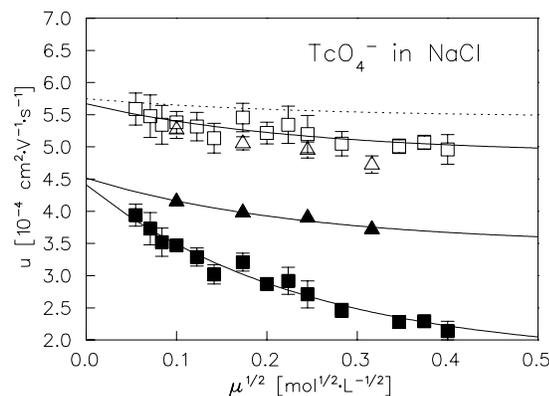


Fig. 4. Individual ion mobility of [^{99m}Tc]TcO₄⁻ at different ionic strength values in aqueous NaCl solutions, at 298.1 K, for a migration tube with an inner diameter of 3 mm. Experimental data with the untreated tube (close squares); data corrected for electroosmosis (open squares); experimental data with the tube coated with polyacrylamide, (close triangles), data corrected for adsorption (open triangles); extended limiting law (dotted line).

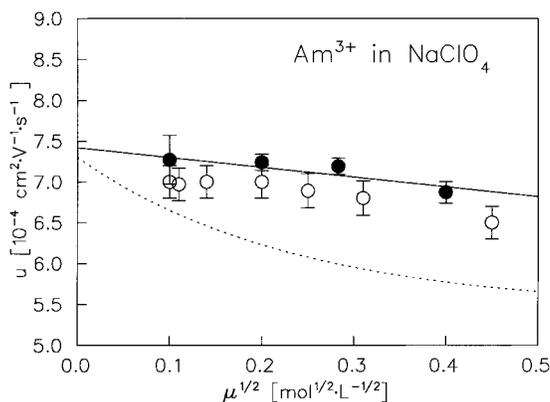


Fig. 5. Individual ion mobility of $[^{241}\text{Am}]\text{Am}^{3+}$ at different ionic strength values in aqueous NaClO_4 solutions at 298.1 K for a migration tube with an inner diameter of 3 mm. Experimental data with the tube coated with TMCS (close circles); data from Rösch *et al.* [9] (open circles); extended limiting law (dotted line).

filled (inner diameter $\phi = 3, 4$ or 5 mm, length $L = 500$ mm) with an electrolyte of given composition. To exclude convective flows of liquid, the migration tube was connected to the electrode cells via hydrodynamics resistors. An electric field intensity of 5 or 10 V cm^{-1} was applied over the migration zone by the use of Pt-electrodes immersed in the electrode cells. In order to ensure a constant electrolyte composition and pH in the migration tube, the electrolyte solution in the electrode cells was continuously refreshed by means of a peristaltic pump. The electromigration experiments were carried out at a temperature of 298.1(5) K using an appropriate thermostating system. The migration of the ions was studied over a period of 30 minutes or 1 hour by continuously scanning the migration tube using a single BGO-detector for the detection of ^{99m}Tc , ^{137}Cs and ^{241}Am and an annular BGO-detector for the detection of ^{18}F and ^{57}Co . In the case of ^{18}F the annular BGO-detector was working in coincidence mode. A scanning increment of 0.2 mm, a counting time of 100 ms per channel and a value of 20% of the maximum distribution for the left and right scanning limits were set. The experiments were performed in non-coated and coated tubes.

Coating of the migration tube

In order to eliminate the electroosmosis, two coating procedures were tested. In the first one the migration tube was simply silanated with a 30% trimethylchlorosilane (TMCS) solution in benzene for 24 hours at room temperature, rinsed with benzene and dried in an oven at 80° for about 6 hours to eliminate residues of benzene. In the second procedure, the tube was coated with a mono-molecular layer of non-cross-linked polyacrylamide (PAC) according to [7] using 3-(trimethoxysilyl)propylmethacrylate, N,N,N',N'-tetramethylethylenediamine (TEMED), acrylamide and potassium peroxodisulfate.

Nuclides and chemicals

The no-carrier-added radioisotopes ^{99m}Tc , ^{18}F , ^{137}Cs , ^{57}Co and ^{241}Am were used for the investigations. Solutions of ^{99m}Tc as sodium pertechnetate with a specific volume activity of about 100–200 MBq/ml ($\sim 10^{-12}$ mol/ml) were

obtained from a $^{99}\text{Mo}/^{99m}\text{Tc}$ -generator (ElutecTM Dupont Pharma S.A.) by elution with 3 ml of 0.9% NaCl solutions. Stock solutions of ^{18}F of 30–80 GBq/ml produced via the (p,n)-reaction on ^{18}O -enriched water were supplied by EURO-PET Freiburg. Stock solutions of ^{137}Cs (400 MBq/ml, 1 M HCl) and ^{57}Co (80 MBq/ml, 1 M HCl) were provided by CSI Diagnostik GmbH. Aliquots of the stock solutions were diluted with deionised water to obtain a specific volume activity of 1000–3000 kBq/ μl for ^{18}F ($\sim 10^{-15}$ mol/ μl) and 200–300 kBq/ μl for ^{137}Cs ($\sim 10^{-10}$ mol/ μl) and ^{57}Co ($\sim 10^{-12}$ mol/ μl). In the case of ^{241}Am , solutions with a specific volume activity of 40–60 kBq/ μl ($\sim 10^{-9}$ mol/ μl) were prepared from a stock solution which was purified on a chromatographic column filled with anion exchange resin Dowex AG1-X8 (< 400 mesh).

The electrolyte solutions of NaCl and NaClO_4 with concentrations in the range 0.001–0.16 M were prepared from deionised water and analytical grade chemicals without further purification.

Data analysis

At the beginning of the experiment ($t = 0$ to 5 min) the activity distribution in the migrating zone could be depicted by a symmetric Gaussian, which gradually changes into an asymmetric form as the electromigration goes on due to electromigration dispersion (unsteady-state migration) [7]. For a time greater than 5 minutes the shape and the height of the asymmetrical distributions were constant. The absolute position of the ions was determined by the analysis of the distributions with a Gaussian setting a preferential fit on the front of the migration [1]. The experimental migration velocity of the ions, v_{exp} , was calculated on-line from the slope of the linear relation obtained between the position of the ions and the time. The experimental individual ion mobility, u_{exp} , was obtained by dividing v_{exp} with the intensity of the electric field. Each value of u_{exp} reported in the present study is an average of two to five independent measurements with a precision ranging between 0.5 and 2%. The standard deviation on the average value lies between 2 and 4%.

Results and discussion

Electromigration in non-coated tubes

The variation of u_{exp} with the overall ionic strength of the electrolyte μ is shown for Cs^+ , Co^{2+} , F^- and TcO_4^- ions in Figs. 1–4 for the measurements carried out with the untreated migration tubes. The individual ion mobility decreases with increasing overall ionic strength which is qualitatively in agreement with the Onsager theory. The experimental individual ion mobility at infinite dilution of the electrolyte ($\mu = 0$), u_{exp}^0 , was obtained by fitting the data with the following relation:

$$u_{\text{exp}} = u_{\text{exp}}^0 - k_{\text{exp}} \times \frac{\sqrt{\mu}}{(1 + A\sqrt{\mu})(1 + B\sqrt{\mu})} \quad (8)$$

where A and B are fixed to 1.328 and 0.939 and to 1.305 and 0.923 for the migration in NaClO_4 and NaCl electrolyte respectively. k_{exp} is a specific constant of the system resulting

Table 2. Experimental individual ion mobilities at infinite dilution of the electrolyte u_{exp}° and coefficients k_{exp} for the ions studied with untreated migration tubes of various inner diameter ϕ . u_{abs}° : individual ion mobility at infinite dilution of the electrolyte; u_{osm}° : experimental electroosmotic ion mobility at infinite dilution of the electrolyte from relation (10); u° : individual ion mobility at infinite dilution of the electrolyte from the literature (see Table 1); k : coefficient from the extended limiting law, k_{abs} : experimental coefficient corrected from the electroosmosis.

Ion	u°	k	$\phi = 3 \text{ mm}$				$\phi = 4 \text{ mm}$				$\phi = 5 \text{ mm}$				
			u_{exp}°	k_{exp}	u_{osm}°	k_{abs}	u_{exp}°	k_{exp}	u_{osm}°	k_{abs}	u_{exp}°	k_{exp}	u_{osm}°	k_{abs}	u_{abs}°
Cs ⁺	8.00	2.16	10.49(10)	9.98(1.17)	2.49(10)	2.37(29)	–	–	–	–	–	–	–	–	7.95(11)
Co ²⁺	5.70	3.15	8.32(9)	14.31(60)	2.62(9)	4.50(25)	8.12(6)	15.40(47)	2.42(6)	4.59(18)	7.94(20)	14.66(1.41)	2.24(20)	4.13(55)	5.76(8)
F [–]	5.74	1.28	4.62(29)	7.28(1.89)	1.12(29)	1.76(65)	4.57(7)	6.88(54)	1.17(7)	1.76(17)	4.76(13)	7.12(98)	0.98(13)	1.46(28)	5.70(7)
TcO ₄ [–]	5.75	1.23	4.41(9)	11.42(65)	1.34(9)	3.47(31)	–	–	–	–	–	–	–	–	5.65(8)

u° , u_{exp}° , u_{abs}° , u_{osm}° in $10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$;
 k , k_{exp} , k_{abs} in $10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1} \text{ mol}^{-1/2} \text{ L}^{-1/2}$.

from the fit. Compared with the literature data u° , the values of u_{exp}° are higher for the cations and lower for the anions (Table 2). The coefficients k_{exp} are higher compared with the calculated ones (k) according to relation (1) (Table 2).

The discrepancies between the experimental and theoretical values are mainly due to the presence of an electroosmotic flow in the migration tube since no migration of the ions was observed when the intensity of the electric field was set to zero. Electroosmosis can be explained by the presence of an electric double layer at the charged surface of the glass (ionization of surface silanol groups at the inner surface of the migration tube). These negative surface charges are neutralized by the cations of the inert electrolyte in the diffuse layer. Under the influence of an electric field, the hydrated cations of the inert electrolyte in the double layer migrate to the cathode moving the bulk solution by viscous drag. As a result, the cations migrate faster and the anions slower than expected. The electroosmotic mobility depends on the potential at the glass/solution interface and on the concentration and nature (viscosity, dielectric constant, pH) of the electrolyte [8].

In order to obtain absolute migration data, u_{abs} , the experimental individual ion mobility for a given ionic strength of the electrolyte was mathematically corrected from the electroosmosis as follows:

$$u_{\text{abs}} = u_{\text{exp}} \pm u_{\text{osm}}^{\circ} + \left(1 - \frac{u_{\text{osm}}^{\circ}}{u_{\text{exp}}^{\circ}}\right) k_{\text{exp}} \times \frac{\sqrt{\mu}}{(1 + A\sqrt{\mu})(1 + B\sqrt{\mu})} \quad \begin{array}{l} (-\text{cations}) \\ (+\text{anions}) \end{array}, \quad (9)$$

where

$$u_{\text{osm}}^{\circ} = |u_{\text{exp}}^{\circ} - u^{\circ}| \quad (10)$$

represents the experimental electroosmotic mobility at infinite dilution of the electrolyte (Table 2). The third term on the right side of expressions (9) is a correction factor which takes into account the variation of electroosmotic mobility with the ionic strength. According to relation (8), expression (9) may be rewritten:

$$u_{\text{abs}} = u_{\text{exp}}^{\circ} \pm u_{\text{osm}}^{\circ} - k_{\text{abs}} \times \frac{\sqrt{\mu}}{(1 + A\sqrt{\mu})(1 + B\sqrt{\mu})} \quad (11)$$

with $k_{\text{abs}} = k_{\text{exp}} \times (u_{\text{osm}}^{\circ}) / (u_{\text{exp}}^{\circ})$ the corrected specific constant of the system. The values of k_{abs} obtained are close to the expected values k excepted for the TcO₄[–] ion (Table 2).

From the experimental data u_{exp}° , different values of u_{osm}° between cations and anions were obtained (Table 2). This difference is difficult to explain since the same absolute value of u_{osm}° was expected for both cations and anions. However we could remark: a) the values of u_{osm}° are homogeneous within each group of ions (cations/anions) and b) the ratio $u_{\text{osm}}^{\circ} / u_{\text{exp}}^{\circ}$ has the same value for all ions (mean value, 0.27(4)). Since the values of u_{osm}° for the cations were found about two times higher than these for the anions, an overall mean value for u_{osm}° was used for all the ions introducing a weighting factor n depending of the type of ion ($n = 1$ for the anions and $n = 2$ for the cations). The introduction of the factor n is just an academic approach to allow an uniform expression of the relation (9). Based on the analysis of the individual values of u_{osm}° given in Table 2, the following overall mean values: $u_{\text{osm}}^{\circ} = n \times 1.25(10) \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ ($\phi = 3 \text{ mm}$), $u_{\text{osm}}^{\circ} = n \times 1.19(3) \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ ($\phi = 4 \text{ mm}$) and $u_{\text{osm}}^{\circ} = n \times 1.05(10) \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ ($\phi = 5 \text{ mm}$), were used for the correction for electroosmosis.

The decrease of u_{osm}° for increasing values of the inner diameter ϕ of the migration tube (factor of correlation of -0.97) could be associated to a relative diminution of the thickness of the double layer at the charged surface of the glass.

The derived individual ion mobilities, u_{abs} , obtained by applying relation (9) are in close agreement with the theoretical values given by the extended limiting law (Figs. 1–4). The extrapolation of these data to $\mu = 0$ leads to the values of the absolute individual ion mobility at infinite dilution, u_{abs}° (Table 2), which agree well with the literature values u° . From these results, expression (9) can be assumed to give a fairly good correction for electroosmosis, but it may be subject to some criticism because of its semi empirical form.

Electromigration in coated tubes

In order to eliminate the electroosmosis occurring in the non-coated tubes, the migration tubes were silanated with TMCS or PAC. The silanation with PAC was found to be more stable over time than the silanation with TMCS. As shown in Figs. 1,2, the experimental values obtained for Cs⁺ and Co²⁺ after the silanation are in close agreement with the theoretical values and with the values calculated from expression (9), indicating thus an efficient suppression of electroosmosis. In addition, the values of the individual ion mobility of Am³⁺ ions measured in NaClO₄ at various concentrations with a silanated glass tube encompass well the data obtained by Rösch *et al.* [9] (Fig. 5). The ion mobility of Am³⁺

Table 3. Ion mobility of Am^{3+} at infinite dilution of the electrolyte determined by different methods at 298 K.

u° $10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$	Experimental method	[Ref.]
7.30(20)	Electromigration in free electrolyte	[9]
7.30(3)	Open end capillary method	[12]
7.23(6)	Open end capillary method	[16]
6.67(15)	Conductivity measurement	[17]
6.96(7)	Electromigration on paper	[18]
6.87(–)	Electromigration on paper	[19]
7.41(9)	Electromigration in free electrolyte	this work

at infinite dilution agrees well with the data obtained by different methods (Table 3).

However, as shown in Figs. 3,4, the experimental data for the anions F^- and TcO_4^- , though higher than these obtained without silanation of the tube, are still lower than expected. In this case the migration of the anions was affected by the adsorption/interaction of the ions with the polyacrylamide layer. Assuming this effect independent of the ionic strength of the electrolyte, the absolute migration data for F^- and TcO_4^- were obtained dividing the experimental values by a retention factor defined as:

$$R = \frac{u_{\text{exp}}^\circ}{u^\circ} \quad (12)$$

where u_{exp}° is the experimental individual ion mobility at infinite dilution of the electrolyte ($u_{\text{exp}}^\circ = 4.20(4) \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ for F^- ; $u_{\text{exp}}^\circ = 4.52(8) \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ for TcO_4^-) and u° the expected value. The resulting retention factors are $R = 0.73(1)$ for F^- and $R = 0.79(1)$ for TcO_4^- . As shown in Figs. 3,4 the corrected migration data encompass well the data obtained after correction of the electroosmosis.

Ion mobility

The results obtained for the Cs^+ and Co^{2+} ions show that the extended limiting law reproduces well the variation of the ion mobility of these ions with the overall ionic strength of the inert electrolyte. The applicability of the extended limiting law for electrolyte concentrations lower than 0.1 M was previously observed for Cs^+ from the measurement of diffusion coefficients of Cs^+ in $\text{CsCl-H}_2\text{O}$ system [10] and for Co^{2+} from the measurement of diffusion coefficients of Co^{2+} in various aqueous electrolyte solutions [11]. In the case of Am^{3+} , the absolute individual ion mobilities are found higher than the values predicted by the extended limiting law. The same type of deviation may be observed for the lanthanide ions from their diffusion coefficients in LiCl ($0.006 \text{ M} < c < 0.5 \text{ M}$) [12] and from their ion mobilities in NaClO_4 ($c = 0.1 \text{ M}$) [9] electrolytes.

The ion mobility of F^- ions is well described by the extended limiting law. In the case of TcO_4^- , the absolute

migration data are found lower than the theoretical values. A detailed analysis of the conductivity data of KTcO_4 ($c < 0.1 \text{ M}$) at 298 K [13] and of the migration data of TcO_4^- in NaNO_3 and KNO_3 electrolytes ($c < 0.2 \text{ M}$) at 291 K [14] leads to the same observation. A such deviation from the theory could be attributed to the tetrahedral geometry of the TcO_4^- ion since the Onsager theory as well the correction proposed by Stokes are built on the assumption that the ions are spherical. Thus, a break of the spherical symmetry could lead to an increase of the frictional forces exerted on the ion and, hence to a lowering of the ion mobility.

Conclusion

The electromigration device tested in the present work is suitable for the determination of absolute ion mobilities despite the occurrence of electroosmotic effects. As demonstrated in this study, effects of electroosmosis may be mathematically corrected to yield absolute individual ion mobilities. Moreover, electroosmosis can be suppressed by chemical surface modification. If there is no interaction between the migrating species and the tube coating, this approach will be preferred because absolute electromigration data are directly obtained in this case.

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