Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 994 (2003) 199–206
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Determination of the absolute mobility and the equivalent ionic conductivity of NpO_2^+ at 25 °C and at infinite dilution by capillary electrophoresis–inductively coupled plasma-mass spectrometry

J. Aupiais*, A. Delorme, N. Baglan
CEA, DASE/RCE, BP 12, 91680 Bruyères-le-Châtel, France

Received 17 December 2002; received in revised form 12 February 2003; accepted 10 March 2003

Abstract

The absolute mobility of NpO_2^+ and its equivalent ionic conductivity were extrapolated at 25 °C and at infinite dilution using a set of experimental data obtained at various ionic strengths. The separation was carried out by capillary electrophoresis (CE) at various concentrations of creatinine at a pH of 5. The detection of NpO_2^+ was performed by inductively coupled plasma mass spectrometry coupled on-line with CE. The following values have been found: $\mu^0_{NpO_2^+}(25\,°C)=(2.94\pm0.07)\cdot10^{-4}$ cm^2 V^{-1} s^{-1} and $\Lambda^0_{NpO_2^+}$ ($\times10^4$, 25 °C)$=28.3\pm0.7$ m^2 S mol^{-1}.

Keywords: Electrophoretic mobility; Temperature effects; Ionic strength; Neptunium

1. Introduction

Nowadays, the speciation of radionuclides or chemical pollutants becomes a subject of interest especially for predicting their behaviour in the biosphere and their potential impact on health [1–3]. Indeed, the migration in the environment and the toxicity depend on the chemical species with respect to the thermodynamic conditions encountered in nature such as pH, pE, ionic strength and temperature [4]. In order to predict the behaviour of radionuclides in the environment, it is necessary to get thermodynamical constants for natural complexing ligands such as humic and fulvic acids or inorganic anions such as phosphate, sulphate and carbonate [5].

Furthermore, when focusing particularly on radionuclides, the radioactivity levels encountered in the environmental samples are generally very low [6–13]. Moreover, some authors have demonstrated experimentally that the thermodynamical constants of some elements at ultra trace level (e.g. below pg/g), which is supposed to be independent of the metal concentration in case of large excess of ligand, could vary with respect to their concentrations [14]. Therefore, the very low concentration of these radionuclides and their repartitions in several chemical species necessitate the use of a sensitive detector while the separation of different species necessitates efficient separation techniques with high separation factors. Coupling of a mass spectrometer with capillary electrophoresis (CE) is a judicious combination for such a purpose [1,5,15–17]. Thus, we have coupled a fast and efficient separation (CE) with a

*Corresponding author. Fax: +33-1-6926-7065.
E-mail address: jean.aupiais@cea.fr (J. Aupiais).

0021-9673/03/$ – see front matter
doi:10.1016/S0021-9673(03)00453-9

very sensitive detection method (inductively coupled plasma mass spectrometry, ICP-MS) [18] for which the achieved detection limit is about 1 fg/g. The use of CE–ICP-MS is justified, on one hand, because ICP-MS is not able to directly detect the chemical species of any elements because their chemical structures are destroyed in the Ar plasma (7000 K), and on the other hand, CE is not able to detect metal concentration below 10^{-8} *M* with the detection methods commonly used with it [19–21]. The univocal attribution of a peak to an element is then only possible if the reproducibility in terms of migration time is high enough to identify any peak without ambiguity. In order to build up a database gathering all electrophoretic mobilities connecting to radionuclides at ultra trace level, it becomes necessary to determine with sufficient accuracy the absolute mobility of all species of interest. We have developed a procedure which can get the absolute mobility extrapolated at infinite dilution. The theory will be shortly presented and the first determination of the absolute mobility of Np(V) at low concentration will be presented.

2. Experimental

2.1. Electrolyte preparation

Various masses of creatinine were dissolved in a 50-ml flask in order to get final concentrations ranging from 5 to 150 m*M*. After dissolution, the pH was adjusted with concentrated $HClO_4$ to get a final pH of 5.00. This pH value allows a buffer capacity of creatinine since its pK_a is equal to 4.85. The solution was filtered through a 0.45-μm Millipore filter.

2.2. Sample preparation

Separations were carried out using a stock solution of NpO_2^+ in 4 *M* HNO_3 ($C=0.637$ mg/l) and two standard solutions of Cs^+ ($C=5$ mg/l) and Li^+ ($C=20$ mg/l) prepared with standard solutions at 1 g/l supplied by Spex (Metuchen, NJ, USA). Samples were prepared according to the following procedure: 200 μl of Np(V) stock solution, 100 μl of Cs diluted solution and 100 μl of Li diluted solution were evaporated to dryness in the same beaker. The residue is dissolved in 100 μl 70% $HClO_4$ and then evaporated to dryness. These dissolution–evaporation steps were performed three times. Finally, the last residue was dissolved in the corresponding electrolyte and the sample filtered through a 0.45-μm Millipore filter.

2.3. Electrophoresis

Electrophoretic separations were performed with a Beckman capillary electrophoretic system (Fullerton, CA, USA). ICP-MS detection was carried out with a Fisons Instruments PlasmaQuad 2+ (VG elemental, Winsford, UK). The interface between CE and ICP-MS is a laboratory-made metal piece [22] ensuring a constant flow-rate at 50 μl/min up to the plasma torch, as well as the electrical ground.

2.4. Electrophoretic conditions

Separations were carried out with a fused-silica capillary (70 cm×75 μm I.D.). The applied voltage is not constant between each set of experiments and varies from 15 kV ($I=20$ m*M*) to 4 kV ($I=150$ m*M*) according to the Ohm's law. Indeed, depending on the ionic strength, the dissipating heat must be kept under control in order to avoid the variation of the internal resistance of the electrolyte during the run. The applied voltage for each ionic strength is the highest possible voltage for which the Ohm's law is valid. Thus the following voltages were applied: 20 and 35 m*M*, $V=15.1$ kV, 50 m*M*, $V=10.1$ kV, 75 m*M*, $V=7$ kV, 100 m*M*, $V=5$ kV and 150 m*M*, $V=4$ kV. Before each set of experiment, the capillary was rinsed with 0.1 *M* HCl for 15 min, then water for 5 min and 0.25 *M* NaOH for 60 min. The stabilisation of the electroosmotic flow (eof) with the electrolyte is achieved after 20 h ($I=50$–150 m*M*), 30 h ($I=10$–50 m*M*). Temperature was maintained at 25.0 °C by cooling with a water circuit surrounding the capillary. Nine experiments were carried out per each ionic strength.

3. Theoretical

The apparent mobility of an ion *i* can be ex-

perimentally determined from its migration time t_m and the migration time of electroosmotic flow t_{eof} according to the relation:

$$\mu_{app} = \frac{Ll}{V} \cdot \left(\frac{1}{t_m} - \frac{1}{t_{eof}} \right) \quad (1)$$

where L is the total length of the capillary ($L = 70$ cm), l is the length to detector, and V is the applied voltage. In the case of a coupling CE–ICP-MS, the lengths l and L are equal, so:

$$\mu_{app} = \frac{L^2}{V} \left(\frac{1}{t_m} - \frac{1}{t_{eof}} \right) \quad (2)$$

The determination of the migration time of electroosmotic flow is almost impossible by ICP-MS because there is no neutral marker or inorganic elements co-migrating with the solvent. So, internal markers are required. We have used a fast cation Cs^+ ($\mu_0(Cs) = 8.01\ 10^{-4}$ cm^2 V^{-1} s^{-1} [23]) and a slow one Li^+ ($\mu_0(Li) = 4.01\ 10^{-4}$ cm^2 V^{-1} s^{-1} [23]) in order to match a high range of mobilities, from $\mu^0 \approx 10^{-3}$ to $\approx 10^{-4}$ cm^2 V^{-1} s^{-1}. Under these conditions, it is not possible to calculate an effective mobility, but only a difference of mobility between the ion i and that of the internal markers j according to the relation:

$$\Delta\mu_{app,i,j} = \mu_{app,i} - \mu_{app,j} = \frac{L^2}{V} \cdot \left(\frac{1}{t_i} - \frac{1}{t_j} \right) \quad (3)$$

3.1. Temperature effect

It is known that mobility depends on temperature [19,24]. The mobility decreases by about 2%/K [25]. This behaviour is due to Joule heating and must be kept under control for the determination of the absolute mobility which also depends on the temperature. Several methods are available for the estimation of the temperature excess [25–28]. Due to the impossibility of determining the mobility of the electroosmotic flow by CE–ICP-MS, we have focused on two methods [19,25]. Knox has defined the temperature excess in the core of the capillary (i.e. the difference the temperature on the axis of the tube and its inner wall) as:

$$\theta_{core} = \frac{E^2 \lambda c \varepsilon d_c^2}{16 \kappa_{TH}} \quad (4)$$

with E the electric field (in V m^{-1}), λ the molar conductivity (in m^2 mol^{-1} Ω^{-1}), c the electrolyte concentration (in mol m^{-3}), ε the total porosity of the medium ($\varepsilon = 0.8$ for an open tube), d_c the internal diameter of the capillary (in m), κ_{TH} the thermal conductivity (in W m^{-1}K^{-1}).

According to the relation $\lambda c = \kappa$ (κ is the conductivity of the solution, in m^{-1} Ω^{-1}), the Eq. (4) becomes:

$$\theta_{core} = \frac{E^2 \kappa \varepsilon d_c^2}{16 \kappa_{TH}} \quad (5)$$

The conductivity κ at a reference temperature (for instance 25 °C) for a given electrolyte can be determined by finding the intercept κ_0 on a graph where the power per meter P ($P = iV/L$), i being the current, V the applied voltage, L the length of the capillary) is plotted against the conductivity ($\kappa = iL/1/4\pi d_c^2 V$) [19].

This method also allows the determination of the temperature excess inside the capillary according to the relation [19]:

$$\Delta T = \frac{riV}{L} \quad (6)$$

with

$$r = \frac{1}{0.02} \cdot \frac{\text{slope}\,(P,\kappa)}{\kappa_0} \quad (7)$$

Both Eqs. (5) and (6) will be compared and contrasted in the following section.

3.2. Pitt's equation

According to Li et al. for the prediction of electrophoretic mobility, the application of the Pitt's equation is necessary to avoid discrepancy in the determination of the electrophoretic mobilities and their comparisons with reference data obtained by other means [29]:

$$\mu_i = \mu_i^0 - (a_1 z_i^2 + a_2 z_i^2 \mu_i^0) \cdot \frac{\sqrt{I}}{1 + Ba\sqrt{I}} \quad (8)$$

where a_1 and a_2 are constant, z_i is the ionic charge of the ion i, μ_i^0 is its absolute mobility at infinite dilution and Ba a constant for which the parameter a is the mean distance of closest approach for the ion i

and B a constant depending on the temperature [30]. For instance, B is equal to 0.3291 $Å^{-1}$ $M^{-1/2}$ at 25 °C.

Thus, the difference $\Delta\mu_{\mathrm{app},i,j}$ between an ion i of charge z_i and a internal marker j of charge z_j is, as a function of the ionic strength:

$$\Delta\mu_{\mathrm{app},i,j} = \Delta\mu^0_{i,j} - \left[a_1\Delta z^2_{i,j} + a_2\left(z_i^2\mu_i^0 - z_j^2\mu_j^0\right)\right] \cdot \frac{\sqrt{I}}{1 + Ba\sqrt{I}} \quad (9)$$

Eq. (9) supposes the same Ba value for the ions of the same i and j nature [4,31,32]. For large carboxylic acids Li et al. have empirically proposed the value $Ba = 2.4$ [29]. For small ions, and according to the recommendation of OECD, Ba is equal to 1.5 [4,33]. This value minimises the error for the specific interaction theory (SIT) used for the determination of stability constants from 0.1 to 3.5 molal. On the contrary, Pitzer and Mayorga suggests the value $Ba = 1.2$ [32,34]. We will test both values, but it must be kept in mind that this adjustment is valid for ionic strength of $I \geq 0.1$ M [4,35,36].

Finally, the variation of $\Delta\mu_{\mathrm{app},i,j} = f(I)$ depends on the determination of three parameters: $\Delta\mu^0_{i,j}$, Ba and the term in brackets in Eq. (9). By plotting $\Delta\mu_{\mathrm{app},i,j}$ versus $\sqrt{I}/1 + Ba\sqrt{I}$ a linear relation is expected and the extrapolation at zero ionic strength allows the calculation of the absolute mobility according to the relation:

$$\mu_i^0 = \Delta\mu^0_{i,j} + \mu_j^0 \quad (10)$$

The term in brackets in Eq. (9) also depends on μ_i^0 and μ_j^0, but these parameters are constant and lead to a simple dependence of the slope with the ions studied.

3.3. Debye–Hückel–Onsager's equation

At low concentration of ions ($C_i \leq 10^{-3}$ M) and for a totally dissociated 1:1 electrolyte, the ionic conductivity λ_i is assumed to obey the Debye–Hückel–Onsager's equation [29,37],

$$\lambda_i = \lambda_i^0 - S_i\sqrt{I} \quad (11)$$

Due to a simple relation between the limiting equivalent conductivity and the effective mobility, a linear trend should be observed between the effective mobility and the square root of the ionic strength according to the relation:

$$\mu_i = \mu_i^0 - S_i'\sqrt{I} \quad (12)$$

with $S_i' = S_iF$, where F is the Faraday constant.

Using internal standards j such as Cs^+ or Li^+, the relative mobility of an ion i is:

$$\Delta\mu_{i,j} = \Delta\mu^0_{i,j} - \mathrm{Const}\sqrt{I} \quad (13)$$

Eq. (12) is assumed to be valid up to $I = 0.1$ M according to Ref. [38]. The determination of the absolute mobility is then determined similarly by Eq. (10).

4. Results and discussion

According to the Eqs. (1)–(3), the determination of the mobility implicitly requires a constant eof during the run. A constant eof is generally established after a few runs, which allows an acceptable accuracy of few percent [39–41]. By comparison, the equivalent ionic conductivity is determined by conductimetric studies with a high accuracy, generally better than 1% [37,42]. In order to determine the absolute mobility with a similar precision, we propose a methodology using capillary zone electrophoresis. Several conditions must be satisfied for obtaining a reliable value: (a) no complexing agent is present in the electrolyte solution, (b) the electrolyte itself has no interaction with the cation, (c) the electrolyte must have a buffer capacity to stabilise the eof, (d) the pH of the electrolyte must be compatible with the thermodynamical stability of the hydrated cation, (e) the temperature must be controlled. The absence of complexing agent is made possible by using the well-known perchlorate anion as counter-ion. Moreover, if a cationic molecule with a buffer capacity such as amines is employed, no interaction should be observed under the cationic form with the studied cation. Finally, the pH of the electrolyte must be compatible with the hydrated cation stability zone (with respect to hydrolysis). Thus, to determine the absolute mobility of neptunyl(V) cation, the pH of the electrolyte must be <9 [30]. We chose creatinine as the main electrolyte

buffer with a $pK_a = 4.85$ [43] because although rare stability constants are available, this molecule does not present an affinity for alkaline earth compounds [44]. We suppose a similar behaviour for the alkali metals Li and Cs. In order to verify the conditions described previously (a–d), 1-naphthylamine was also tested ($pK_a = 3.92$ [23]). It is assumed that no complexation occurs with alkaline earth or with neptunyl ions. Thus, near pH 4 −5, Np(V) is far from the hydrolysis region and is present as hydrated NpO_2^+. Under optimal conditions, a typical electropherogram is obtained (Fig. 1) showing the capability to detect and separate Np from Cs and Li.

The advantage of the amines is that the ionic strength can be easily adjusted by adding perchloric acid up to the desired pH value. The protonation rate and its total concentration directly give the ionic strength.

4.1. Stabilisation of the electroosmotic flow

Even with a buffer capacity, the stabilisation of the eof is not instantaneous as shown in Fig. 2. This figure shows that extreme accuracy can be achieved above about 12 h. In this region, the eof is stabilised at better than 0.5%. For instance, the experimental determination of the eof at pH 5.00 under our conditions are: $(3.039 \pm 0.012) \cdot 10^{-4}$ cm^2 V^{-1} s^{-1} for 100 m*M* creatinine and $(3.038 \pm 0.005) \cdot 10^{-4}$ cm^2 V^{-1} s^{-1} for 25 m*M* creatinine. The relative precisions are 0.39 and 0.16%, respectively.

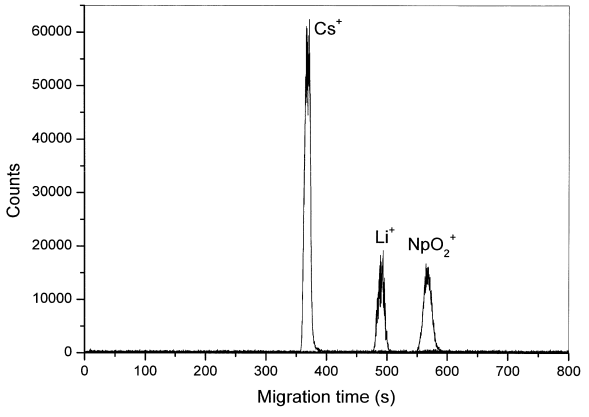

Fig. 1. Electropherogram of Cs^+, Li^+ and NpO_2^+, creatinine–$HClO_4$ 50 m*M*, pH 5.00, *V* = 10.1 kV, *i* = 27 μA, *L* = 70 cm × 75 μm I.D., [Cs^+] = 0.5 μg/ml, [Li^+] = 2 μg/ml, [NpO_2^+] = 0.13 μg/ml.

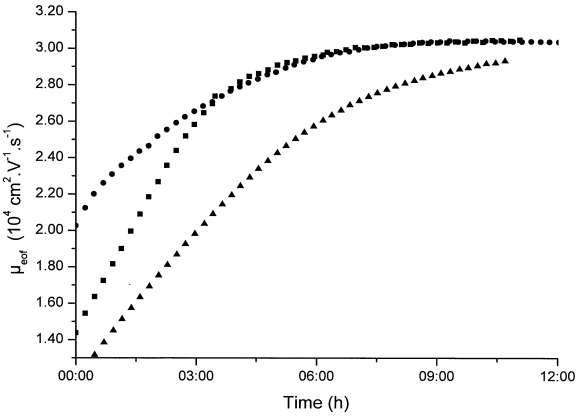

Fig. 2. Temporal evolution of the electroosmotic flow; electrolyte buffer creatinine at pH 5.00 by adding $HClO_4$, capillary 35 cm × 50 μm, indirect detection at 214 nm, electroosmotic flow marker dimethylformamide 0.5% in water, *V* = 20 kV; (●) 25 m*M* creatinine, (▼) 50 m*M* creatinine, (■) 100 m*M* creatinine.

4.2. Temperature effect

According to the procedure described by Kok, we have calculated the conductivity of the electrolyte κ_0 at 25 °C. κ_0 allows the evaluation of θ_{core} (Eq. (5)) and ΔT (Eq. (6)). The results are gathered in Table 1. All sets of data should be corrected accordingly to the relation [19]:

$$\Delta\mu\ (25\ ^\circ\mathrm{C}) = \frac{\Delta\mu\ (T)}{(1 + 0.02 \times \Delta T)} \qquad (14)$$

It is surprising to note a strong discrepancy between the methods. According to Knox [25], the evaluation of the temperature excess makes it pos-

Table 1
Temperature excess calculated according to Eqs. (5) and (6); electrolyte creatinine–$HClO_4$, pH 5.00

c_E (m*M*)	κ_0 (m^{-1} Ω^{-1})	*r*	ΔT (K)	θ_{core} (K)
20	0.179 ± 0.002	6.02 ± 0.40	2.41 ± 0.16	0.04
35	0.292 ± 0.004	5.23 ± 0.39	3.52 ± 0.26	0.07
50	0.404 ± 0.003	4.92 ± 0.15	1.96 ± 0.06	0.04
75	0.603 ± 0.004	5.93 ± 0.41	1.70 ± 0.12	0.03
100	0.761 ± 0.002	6.11 ± 0.37	1.11 ± 0.15	0.02

sible to neglect this contribution because the corrections are largely within the experimental errors. On the contrary, according to Kok [19], the temperature excess is not negligible and the temperature correction must be calculated.

Thus, by applying these corrections for the determination of the absolute mobility of Li^+ (internal marker Cs^+) of five points for which temperature excess have been determined, the intercept of the linear regression gives $\mu^0_{Li} = (4.37 \pm 0.29) \cdot 10^{-4}$ cm^2 V^{-1} s^{-1} (correlation $r = 0.978$), while for the raw data (without temperature excess correction), the intercept is equal to $\mu^0_{Li} = (3.95 \pm 0.14) \cdot 10^{-4}$ cm^2 V^{-1} s^{-1} ($r = 0.999$) (see Fig. 3), compared to the recommended value [23] $\mu^0_{Li} = 4.01 \cdot 10^{-4}$ cm^2 V^{-1} s^{-1}. Similar results have been obtained by Li et al. [29] since his results, determined with an error of about 3% without temperature correction, are in good agreement with other determinations. His conditions are very similar to ours, which means that the temperature excess inside the capillary is negligible. Indeed, using all data in Fig. 3 ($n = 8$ points, creatinine and 1-napthylamine buffers), the absolute mobility of Li is then equal to $\mu^0_{Li} = (3.95 \pm 0.07) \cdot 10^{-4}$ cm^2 V^{-1} s^{-1} ($r = 0.999$). The uncertainty (± 0.07; i.e. about 2%) has the same value than the temperature dependence of the electrophoretic mobility (2%/K). Therefore the temperature excess cannot be exceed 1 K.

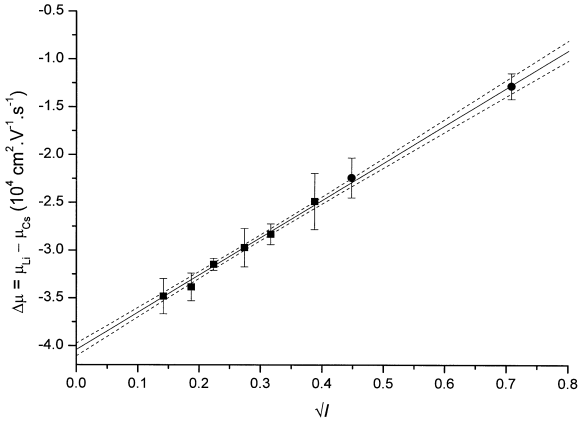

Fig. 3. Variation of $\Delta\mu_{Li,Cs} = \mu_{Li} - \mu_{Cs}$ as a function of the square root of the ionic strength; (■) creatinine–$HClO_4$, pH 5.00, at various concentration of creatinine, (●) 1-naphthylamine 7 mM–$HClO_4$–$NaClO_4$, pH 4.00, at various concentration of $NaClO_4$; capillary 70 cm×75 μm; voltage see Experimental; intercept = $-(-4.04 \pm 0.07) \cdot 10^{-4}$ cm^2 V^{-1} s^{-1}; slope = $(3.92 \pm 0.56) \cdot 10^{-4}$ cm^2 V^{-1} s^{-1} M$^{-1/2}$; $r = 0.999$, 95% confidence level.

It becomes obvious that the method described by Kok overestimates the temperature excess inside the capillary. In conclusion, the use of two internal markers with well defined absolute mobility demonstrates, by extrapolating at zero ionic strength, the possibility to check the experimental data against any elevation of the temperature.

4.3. Ionic strength effect

In order to determine the better representation of the mobility in a function of the ionic strength, we have plotted in Fig. 4, the variation of $\Delta\mu$ as a function of $\sqrt{I}$, $\sqrt{I}/1 + 1.2\sqrt{I}$, and $\sqrt{I}/1 + 1.5\sqrt{I}$. The data have not been corrected for temperature according to the previous discussion. Fig. 4 shows that a simple relationship in $I^{1/2}$ is sufficient within the experimental errors to predict the variation of the mobility up to 0.5 M. This unexpected behaviour to the conventional theories involving the closest approach of an ion must be discussed. We shall not question the actual theory, but under electrophoretic conditions, the Debye–Hückel–Onsager's model is valid up to 0.1 M for small cations with high density of charge and spherical symmetry [29] (which is naturally the case for Li^+ and Cs^+). Moreover, since the ionic strength is the main relevant parameter altering the mobility, the nature of the electrolyte should have no effect on the results. In the Fig. 3, 2

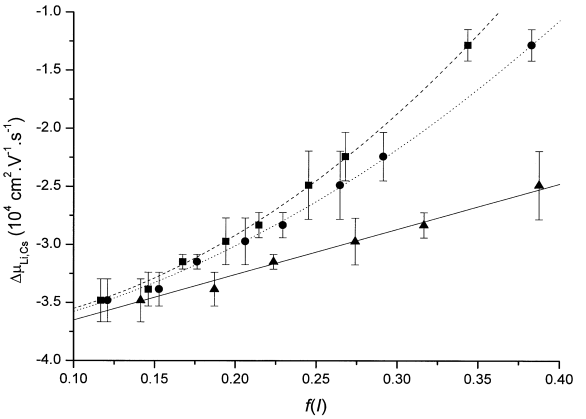

Fig. 4. Variation of $\Delta\mu_{Li,\ Cs} = \mu_{Li} - \mu_{Cs}$ as a function of (■) $\sqrt{I}/1 + 1.5\sqrt{I}$, (●) $\sqrt{I}/1 + 1.2\sqrt{I}$ and (▲) $\sqrt{I}$.

different sets of experiments have been gathered, one using creatinine at pH 5.00 and the second one using 1-naphthylamine at pH 4.00 as cationic buffers. Both data are quite well aligned according to the Debye–Hückel–Onsager's model up to 0.5 *M*. Under our conditions, it is not possible to detect any deviation from the model above 0.1 *M* because our experimental uncertainties are large (10%) at 0.2 and 0.5 *M*. Finally, we have shown that the absolute mobility of Li^+ at 95% confidence level is equal to ($n=8$ points): $\mu^0_{Li}=(3.95\pm0.07)\cdot10^{-4}$ cm^2 V^{-1} s^{-1} ($r=0.999$). The deviation is only equal to -1.5% by comparison to the reference value [$\mu_0(Li^+)=4.01\cdot10^{-4}$ cm^2 V^{-1} s^{-1}] and matches with the experimental uncertainty (±0.07).

In conclusion, as long as the temperature effect remains neglected, a simple relation between $\Delta\mu$ and $I^{1/2}$ is sufficient for small inorganic ions.

4.4. Absolute mobility of Np(V)

Two internal markers are used for the determination of the absolute mobility of Np(V). This approach allows a better determination and allows the verification of the method by the determination of the absolute mobility of one of both markers by using the other as internal marker. The experimental data are gathered in Fig. 5 (marker Cs). The extrapolation at zero ionic strength at 25 °C gives the following results (95% confidence level):

- Marker Cs^+: $\mu^0_{NpO_2^+}=(2.94\pm0.07)\cdot10^{-4}$ cm^2 V^{-1} s^{-1}
- Marker Li^+: $\mu^0_{NpO_2^+}=(2.94\pm0.19)\cdot10^{-4}$ cm^2 V^{-1} s^{-1},

The better precision with caesium is due to a bigger difference between the effective mobility of Np(V) and that of Cs(I). In practice, it is not recommended to use an internal marker with a mobility close to that of the studied species. Therefore, we have chosen the determination having the better accuracy. Thus, the equivalent ionic conductivity at 25 °C is $\Lambda^0_{NpO_2^+}(\cdot10^4)=28.3\pm0.7$ m^2 S mol^{-1}.

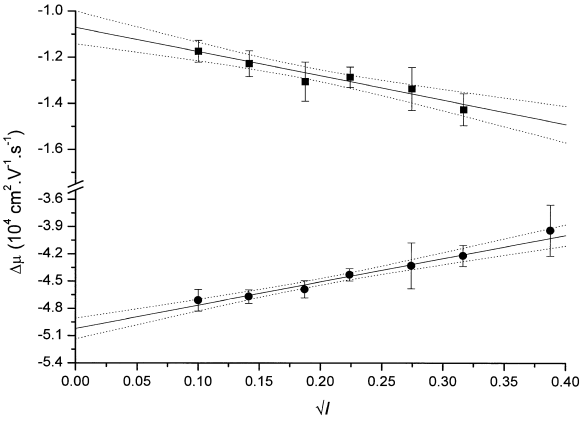

Fig. 5. Variations of $\Delta\mu_{Np,\,Cs}=\mu_{Np}-\mu_{Cs}$ and $\Delta\mu_{Np,Li}=\mu_{Np}-\mu_{Li}$ as a function of $\sqrt{I}$, buffer creatinine, pH 5.00, by $HClO_4$, voltage see Experimental; $n=9$ determinations per point; (●) Cs marker, intercept $=-(5.07\pm0.12)\cdot10^{-4}$ cm^2 V^{-1}s^{-1}; slope $=(2.75\pm1.33)\cdot10^{-4}$ cm^2 V^{-1} s^{-1} M$^{-1/2}$; $r=0.979$, 95% confidence level. (■) Li marker, intercept $=-(1.07\pm0.07)\cdot10^{-4}$ cm^2 V^{-1} s^{-1}, slope $=-(1.05\pm0.66)\cdot10^{-4}$ cm^2 V^{-1} s^{-1} M$^{-1/2}$; $r=0.972$, 95% confidence level.

5. Conclusion

The determination of the absolute mobility of Np(V) has been achieved using the Debye–Hückel–Onsager's equation without any complexing electrolyte. This approach allows a very high accuracy of about 2% if the capillary is stabilised by the electrolyte for at least 12 h. From a theoretical point of view, it seems that the Debye–Hückel–Onsager's model is valid slightly above 0.1 *M* for small ions for which a high density of charge and a spherical symmetry is expected.

References

[1] J.W. Olesik, in: J.A. Caruso, K.L. Sutton, K.L. Ackley (Eds.), Comprehensive Analytical Chemistry, Elsevier, Amsterdam, 2000, p. 151.
[2] R.E. Clement, P.W. Yang, Anal. Chem. 73 (2001) 2761.
[3] S.D. Richardson, Anal. Chem. 73 (2001) 2719.
[4] I. Grenthe, I. Puigdomenech, Modelling in Aquatic Chemistry, OECD, Paris, 1997.
[5] E. Dabek-Zlotorzynska, E.P.C. Lai, A.R. Timerbaev, Anal. Chim. Acta 359 (1998) 1.
[6] Y. Bourlat, J.C. Millies-Lacroix, R. Nazard, J. Radioanal. Nucl. Chem. Articles 197 (1995) 387.
[7] Y. Bourlat, J.C. Millies-Lacroix, G. Le Petit, J. Bourguignon, in I.P.S.N. (Editor), Radionuclides in the Oceans—Inputs and Inventories, Les Editions de Physique, Paris, 1996, p. 75.

[8] W.C. Burnett, D.R. Corbett, M. Schultz, E.P. Horwitz, R. Chiarizia, M.L. Dietz, A. Thakkar, M. Fern, J. Radioanal. Nucl. Chem. 226 (1997) 121.
[9] S.H. Lee, J. Gastaud, J.J. LaRosa, L. Liong Wee Kwong, P.P. Povinec, E. Wyse, L.K. Fifield, P.A. Hausladen, M.L. di Tada, G.M. Santos, J. Radioanal. Nucl. Chem. 248 (2001) 757.
[10] E. Mathew, V.M. Matkar, K.C. Pillai, J. Radioanal. Chem. 62 (1981) 267.
[11] T. Miura, K. Hayano, K. Nakayama, Anal. Sci. 15 (1999) 23.
[12] Y. Muramatsu, S. Uchida, K. Tagami, S. Yoshida, T. Fujikawa, J. Anal. At. Spectrom. 14 (1999) 859.
[13] J.L. Smith-Briggs, E.J. Bradley, Sci. Total Environ. 35 (1984) 431.
[14] A. Seibert, A. Mansel, C.M. Marquardt, H. Keller, J.V. Kratz, N. Trautmann, Radiochim. Acta 89 (2001) 505.
[15] Y. Liu, V. Lopez-Avila, J.J. Zhu, D.R. Wiederin, W.F. Beckert, Anal. Chem. 67 (1995) 2020.
[16] J.J. Corr, J.F. Anacleto, Anal. Chem. 68 (1996) 2155.
[17] J.W. Olesik, J.A. Kinzer, S.V. Olesik, Anal. Chem. 67 (1995) 1.
[18] R. Chiappini, J.-M. Taillade, S. Brébion, J. Anal. At. Spectrom. 11 (1996) 497.
[19] W. Kok, Chromatographia 51 (2000) 89.
[20] S.C. Beale, Anal. Chem. 70 (1998) 279R.
[21] A.R. Timerbaev, W. Buchberger, J. Chromatogr. A 834 (1999) 117.
[22] A. Delorme, N. Baglan, in preparation.
[23] R.C. Weast, M.J. Astle, W.H. Veyer, Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL, 1988.
[24] P. Gareil, Analusis 18 (1990) 221.
[25] J.H. Knox, Chromatographia 26 (1988) 329.
[26] R.F. Cross, J. Cao, J. Chromatogr. A 809 (1998) 159.
[27] H. Zhang, Q. Li, Z. Hu, R. Wang, X. Chen, J. Chromatogr. A 907 (2001) 353.
[28] R.F. Cross, J. Chromatogr. A 907 (2001) 357.
[29] D. Li, S. Fu, C.A. Lucy, Anal. Chem. 71 (1999) 687.
[30] R.J. Lemire, Chemical Thermodynamics of Neptunium and Plutonium, North-Holland, Amsterdam, 2001.
[31] L. Ciavatta, Ann. Chim. 80 (1990) 255.
[32] K.S. Pitzer, J. Phys. Chem. 77 (1973) 268.
[33] L. Ciavatta, Ann. Chim. 70 (1980) 551.
[34] K.S. Pitzer, G. Mayorga, J. Phys. Chem. 77 (1973) 2300.
[35] G.N. Lewis, M. Randall, Thermodynamics, McGraw-Hill, New York, 1961.
[36] W.J. Hamer, The Structure of Electrolyte Solutions, Wiley, New York, 1959.
[37] B. Fourest, L.R. Morss, G. Blain, F. David, J. M'Halla, Radiochim. Acta 69 (1995) 215.
[38] D.A. Dudek, P.S. Fedkiw, Anal. Chem. 71 (1999) 1469.
[39] H. Wätzig, C. Dette, Fresenius J. Anal. Chem. 345 (1993) 403.
[40] P. Jandik, G. Bonn, Capillary Electrophoresis of Small Molecules and Ions, VCH, New York, 1993.
[41] H. Wätzig, M. Degenhardt, A. Kunkel, Electrophoresis 19 (1998) 2695.
[42] B. Fourest, R. Bury, L.R. Morss, J. M'Halla, F. David, J. Sol. Chem. 22 (1993) 151.
[43] R.M. Smith, A.E. Martell, Critical Stability Constants, Plenum Press, New York, 1975.
[44] L.G. Sillen, A.E. Martell, Stability Constants, The Chemical Society, London, 1964.