E6-2003-74

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DETERMINATION OF ION DIFFUSION COEFFICIENTS BY THE ELECTROMIGRATION METHOD

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1. Theoretical

The horizontal zone electrophoresis in free electrolyte is known to be a powerful method for studying of a large number of chemical and physicochemical processes in a solution. The method allows determination of ion mobilities, ionic transport numbers, stability, hydrolysis and kinetic constants. The electromigration method was recently developed for determination of ion diffusion coefficients in aqueous media.

Generally diffusion processes are described by Fick's second law (Bulatov and Lundin, 1984):

$$\frac{\partial C}{\partial t} = -D \frac{\partial^2 C}{\partial x^2} \tag{1}$$

where:

C is the concentration of the specie
t is the time from start of the diffusion
x is the coordinate
D is the diffusion coefficient.

The Fick's equation can be solved at the following boundary conditions, corresponding with the specificity of electrophoretic experiments.

$$C(x,0) = \begin{cases} C_0, |x| < l \\ 0, |x| > l \end{cases}, \tag{2}$$

where:

C_0 is the initial concentration
l is the half-width of the initial distribution zone.

At the boundary conditions given above the general solution of (1) is:

$$C(x,t) = \frac{C_0}{2}\left[erf\left(\frac{l-x}{2\sqrt{Dt}}\right) + erf\left(\frac{l+x}{2\sqrt{Dt}}\right)\right]. \tag{3}$$

It is complicated to process the electrophoretical data according to equation (3), but Fick's second law can be solved correctly at the presence of unlimited media and constant quantity of diffusing species and respectively boundary conditions (Cranc, 1956):

$$C(\infty,t) = 0 \tag{4}$$

$$\int_0^\infty C(x,t) = M_0. \tag{5}$$

In this case for a general solution we found:

$$C(x,t) = \frac{M_0}{2\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right). \tag{6}$$

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The obtained expression represents a Gaussian distribution function with a square standard deviation:

$$\sigma^2 = \frac{1}{n-1}\sum_1^n (\bar{x} - x_i)^2 = \int_0^\infty x^2 \frac{1}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)dx = 2Dt. \tag{7}$$

Hence, the diffusion coefficient D was determined as follows:

$$D = \frac{\sigma^2}{2t}. \tag{8}$$

In case of Gaussian distribution function, the square standard deviation σ^2 is the averaged square distance from the zone center, which particles run for a time t (Chandrasekhar, 1943). The averaged square distance for equation (3) is given by:

$$\bar{r^2} = \frac{1}{2l}\int_0^\infty \left(erf\left(\frac{l-x}{2\sqrt{Dt}}\right) + erf\left(\frac{l+x}{2\sqrt{Dt}}\right)\right)x^2 dx = 2Dt. \tag{9}$$

From (7) and (9), and taking into account the stochastic nature of diffusion processes we consider that Gaussian distribution function (6) can be used for determination of the diffusion coefficients instead Eq. (3) without loss of correctness.

Scanning distribution zone of the investigated isotope at different moments t_1 and t_2 as well as the determination of the respective standard deviations σ_1 and σ_2 allow calculating the diffusion coefficient in accordance with:

$$D = \frac{\sigma_2^2 - \sigma_1^2}{2(t_2 - t_1)}. \tag{10}$$

If the standard deviation of the zone is measured in more than two different moments, the correlation can be fitted linearly in order to increase the precision.

Experimental

A schematic view of the completely automated device for horizontal zone electrophoresis in free electrolyte (Priemyshev *et al.*, 2000) is presented in Fig. 1. Electromigration and diffusion of the investigated radioactive ions take place in a horizontal glass tube with an inner diameter of 3 mm. Temperature of the solution inside electrophoretic cell was set to 25.00 °C and automatically supported constant with accuracy of 0.05 °C. Electrolyte in the electrode cells was continuously refreshed by means of peristaltic pump for counteraction the possible influence of electrolytic processes. In order to avoid any hydrodynamic fluxes, the connection between electromigration tube and electrode cells was done by ϕ=30 nm nucleopore filter. All solutions used were prepared with *aqua bidestilata* and HNO_3 (Suprapure, Merck).
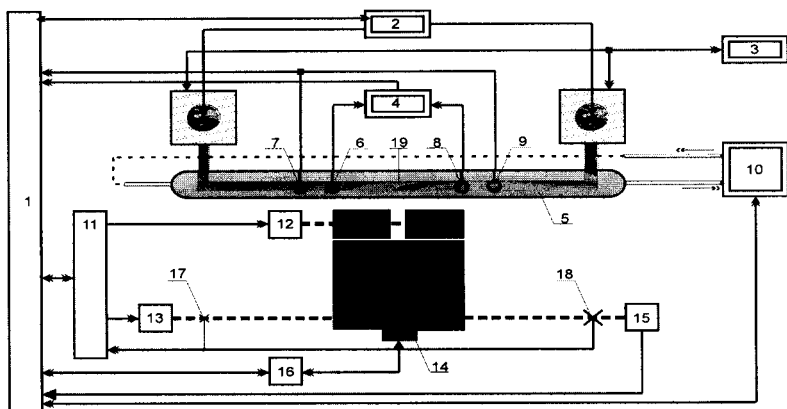
Fig. 1. Schematic view of the electromigration device
1 - PC; 2 - High voltage supply; 3 - Peristaltic pump; 4 - Voltage divider; 5 - Electromigration tube; 6, 8 - Pt electrodes; 7, 9 - Thermosensors; 10 - Thermostat; 11 - Step motors driver; 12, 13 - Step motors; 14 - Gamma-detector CsI(Tl); 15 - Turn gauge; 16 - HV supply; 17, 18 - Edge sensors; 19 - Injection point

Radioisotopes used in the experiments (^{111}In, [175]Hf and [237]Pu) were produced via α,xn reactions on the U-200 cyclotron (FLNR, JINR). The separation of nuclides from the target substance, radiochemical purification and concentration were carried out by the methods of ion-exchange chromatography (Filosofov et al., 2001; Bojikov et al., 2001; Dmitriev et al., 1993). A volume of about 5µl (200-400 kBq) of [111]In(III), [175]Hf(IV) or [237]Pu(VI) containing nitric acid solution was injected into the electrophoretic tube and high voltage was applied. Concentration of the investigated radionuclide in the zone was about 10^{-9}- 10^{-10}M. The active zone was forced to move from the injection point to the homogeneous part of the electromigration tube under the influence of constant electric field gradient of 10 V·cm^{-1}, then the high voltage was switched off and the scanning procedure for determination of diffusion coefficients started. In our experiments electrophoretic cell was continuously scanned for a period of 12-24 h. Under influence of the diffusion processes, the width of active zone increases as it is shown in Figure 2.
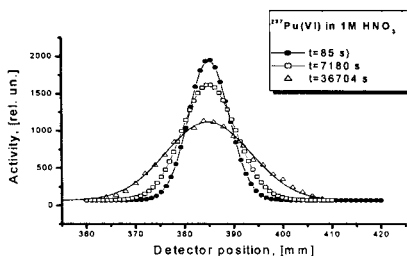

Fig 2. Distribution profiles of [237]Pu(VI) in 0.1M HNO$_3$ at different moments from start of diffusion experiment. Fitting curve is Gaussian function.

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Fitting the distribution profiles gives the standard deviation of the zone as a function of time from start of the experiment.

Fig. 3 shows the dependence between time and zone standard deviation for ^{237}Pu(VI) in 0.1M nitric acid.

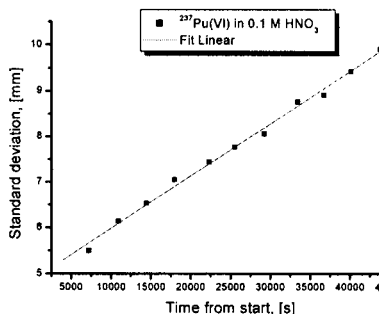Fig 3. Standard deviation- time dependence for ^{237}Pu(VI) in 0.1M HNO$_3$.

After processing the experimental data, according to Eq. (7), diffusion coefficients of the investigated cations in nitric acid solutions were obtained (Table 1).

Table 1. Diffusion coefficients of Cd(II), In(III), Hf(IV) and Pu(VI) in nitric acid media, T=25± 0.05 °C

Ion	Isotope	pH	Diffusion coefficients, cm$^2 \cdot$s^{-1}
In(III)	^{111}In	1.40±0.05	$(7.40\pm0.10)\cdot10^{-6}$
Hf(IV)	^{175}Hf	0	$(7.60\pm0.40)\cdot10^{-6}$
Pu(VI)	^{237}Pu	1.00±0.05	$(8.80\pm0.20)\cdot10^{-6}$

In diluted solutions, with ionic strength lower then 0.01, simultaneously measuring of ion mobility and the diffusion coefficient allows calculation of the effective charge of the studied ions. A relation between electrophoretic mobility and diffusion coefficient is given by the Nernst- Einstein's law (Korita et al., 1975):

$$D = u \frac{RT}{zF},$$
(12)

where:

D is the diffusion coefficient [cm$^2 \cdot$s^{-1}]

R is the gas constant, 8.314 [J·K^{-}1·mol^{-1}]

T is the temperature [K]

z is the effective charge of the ion

F is the Faraday constant, 96484 [Q·mol^{-1}] .

The ion effective charge is only unknown in the equation and can be determined.

In more concentrated solutions, effective ion charge can be only evaluated with a usual occurrence of deviations up to 10-15% (Stepanov and Korchemnaya, 1979).

Conclusions

Electrophoretic method for measuring of ion diffusion coefficients in aqueous solutions is developed. The value of diffusion coefficient can be determined from the linear relationship between square standard deviation of electrophoretic zone and time from start of the diffusion process. Using the device for horizontal zone electrophoresis in a free electrolyte, series of diffusion experiments are performed with no-carrier-added radionuclides in microconcentrations (10^{-9}- 10^{-10}M). Diffusion coefficients of ^{111}In(III), ^{175}Hf(IV) and ^{237}Pu(VI) ions at 25.00 °C are determined in nitric acid media. Simultaneously determination of diffusion coefficient and electrophoretic mobility allows one to calculate the effective charge of investigated ions in accordance with the Nernst- Einstein law.

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Разработан электромиграционный метод измерения ионных диффузионных коэффициентов в водных растворах. Величина диффузионного коэффициента определяется на основе линейной зависимости между среднеквадратичным отклонением электрофоретической зоны и временем от начала эксперимента. При помощи установки для горизонтального зонного электрофореза были измерены коэффициенты диффузии безносительных радионуклидов при 25 °C на уровне микроконцентраций (10^{-9} – 10^{-10} M). Определены коэффициенты диффузии ионов ^{111}In(III), ^{175}Hf(IV) и ^{237}Pu(VI) в азотнокислых растворах.

Работа выполнена в Лаборатории ядерных реакций им. Г. Н. Флерова ОИЯИ.

An electrophoretic method for measuring ion diffusion coefficients in aqueous solutions is developed. The value of the diffusion coefficient can be determined from the linear relationship between the square standard deviation of the electrophoretic zone and the time from the start of the diffusion process. Using the device for horizontal zone electrophoresis in a free electrolyte, a series of diffusion experiments are performed with no-carrier-added radionuclides in microconcentrations (10^{-9} – 10^{-10} M). Diffusion coefficients of ^{111}In(III), ^{175}Hf(IV) and ^{237}Pu(VI) ions at 25 °C are determined in nitric acid media. Simultaneous determination of the diffusion coefficient and electrophoretic mobility allows one to calculate the effective charge of the investigated ions in accordance with the Nernst–Einstein law.

The investigation has been performed at the Flerov Laboratory of Nuclear Reactions, JINR.

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