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G. A. Bozhikov, P. I. Ivanov, G. D. Bontchev*,
O. D. Maslov, M. V. Milanov, S. N. Dmitriev

INVESTIGATION OF CHEMICAL EQUILIBRIUM
KINETICS BY THE ELECTROMIGRATION METHOD

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*Institute for Nuclear Research and Nuclear Energy, 1784 Sofia,
Bulgaria

Introduction

Let us consider a solution with an allocation zone, containing identical particles (ions) formed in it. The allocation of the species is described by the Gaussian distribution function, whose standard deviation increases only under the influence of Brownian motion. If we apply a constant electric field to the solution, all the charged particles will move with a fixed velocity corresponding with their electrophoretic mobility. Since the influence of the electric field gradient is the same for all the identical particles (ions) of the zone, electromigration and diffusion do not interfere with one another and the diffusion coefficient will be unchanged in this case.

However, the situation will change if we consider a zone containing two kinds of particles of different electrophoretic mobility in a chemical equilibrium. The electrophoretic zone will move with an average mobility and suffer an extra expansion due to the unequal electrophoretic velocities of the two kinds of ions concerned. Hence, electrodiffusion causes an additional increase in the zone standard deviation correlated with the reaction rates. In other words, determination of the diffusion and electrodiffusion coefficients will allow calculating the average lifetime and average distance traveled by the particles in a single flight, and finally the kinetic constants of the interaction.

The correlation between equilibrium kinetics and the electrodiffusion effect as well as the possibilities for measuring reaction rates is already discussed [1 – 5].

A device for horizontal zone electrophoresis in a free electrolyte [6] is suitable for study chemical equilibrium processes under undisturbed conditions. Moreover, the electromigration method was recently developed to measure diffusion coefficients in aqueous media [7].

Theory

The electromigration method for measuring reaction rates is based on the stochastic approach [8] to the electrodiffusion random walk theory [1, 2]. Let us consider a chemical reaction of complex formation or hydrolysis equilibrium:

where:

A_1 is a cation form;

A_2 is a complex ion form;

B is a - ligand;

k_1 , k_2 are the rates of the forward and reverse reaction.

For reaction (1), the equilibrium condition can be written as:

$$k_1[A_1][B] = k_2[A_2], \quad (2)$$

where $[A_1]$, $[B]$ and $[A_2]$ denote the equilibrium concentrations of the species.

The kinetic laws for the forward and reverse reactions can be written as:

$$\begin{aligned} \frac{da_1}{dt} &= -k_1[A_1][B]\exp(-k_1[B]t) \\ \frac{da_2}{dt} &= -k_2[A_2]\exp(-k_2t) . \end{aligned} \quad (3)$$

Here a_1 and a_2 are the current concentrations of species A_1 and A_2 , respectively.

Under a constant electric field gradient the common electrophoretic allocation zone moves with an average mobility [9, 10] given by

$$u = \frac{u_1 k_2 + u_2 k_1 [B]}{k_1 [B] + k_2}, \quad (4)$$

where u_1 and u_2 are the electrophoretic mobilities of A_1 and A_2 , respectively. Let us introduce a moving frame of reference which has its origin at the center of zone. In such a manner we consider the relative mobilities of the species (m_1 , m_2) towards the center of the zone:

$$\begin{aligned} m_1 &= \frac{(u_1 - u_2)k_1[B]}{k_1[B] + k_2} \\ m_2 &= \frac{(u_2 - u_1)k_2}{k_1[B] + k_2} . \end{aligned} \quad (5)$$

The distributions of the lifetimes t_i of particles A_i can be retrieved from the kinetic laws:

$$\begin{aligned} \frac{\partial a_1}{\partial t_1} &= k_1[A_1][B]\exp(-k_1[B]t_1) \\ \frac{\partial a_2}{\partial t_2} &= k_2[A_2]\exp(-k_2t_2) . \end{aligned} \quad (6)$$

It is now possible to express the distance x_i with respect to the moving frame of reference covered by a particle A_i in a single lifetime t_i . In a constant electric field, the following relation takes place:

$$x_i = Em_i t_i, \quad (7)$$

where E is the gradient of the electric field. The distributions of lengths is therefore:

$$\begin{aligned} \frac{\partial a_1}{\partial x_1} &= \frac{1}{m_1 E} k_1 [A_1] [B] \exp\left(-\frac{k_1 [B] x_1}{m_1 E}\right) \\ \frac{\partial a_2}{\partial x_2} &= \frac{1}{m_2 E} k_2 [A_2] \exp\left(-\frac{k_2 x_2}{m_2 E}\right). \end{aligned} \quad (8)$$

Computing the average distance covered by the particles of each kind

$$\langle x_1 \rangle = \frac{1}{[A_1]} \int_0^\infty x_1 \frac{k_1 [A_1] [B]}{m_1 E} \exp\left(-\frac{k_1 [B] x_1}{m_1 E}\right) dx_1 \quad (9)$$

$$\langle x_1 \rangle = \frac{m_1 E}{k_1 [B]}$$

$$\langle x_2 \rangle = \frac{1}{[A_2]} \int_0^\infty x_2 \frac{k_2 [A_2]}{m_2 E} \exp\left(-\frac{k_2 x_2}{m_2 E}\right) dx_2 \quad (10)$$

$$\langle x_2 \rangle = \frac{m_2 E}{k_2}$$

one can notice that the average total distance travelled by the particles towards the center of the zone is zero.

$$\begin{aligned} \langle x \rangle &= \langle x_1 \rangle + \langle x_2 \rangle \\ \langle x \rangle &= \frac{m_1 E}{k_1 [B]} + \frac{m_2 E}{k_2} \\ \langle x \rangle &= \frac{E}{k_1 [B] + k_2} [(u_1 - u_2) + (u_2 - u_1)] = 0. \end{aligned} \quad (11)$$

As is shown in [8], this case is equivalent to a diffusion process governed by the diffusion coefficient equal to:

$$D_e = \frac{1}{2} n \langle x^2 \rangle, \quad (12)$$

where n is the mean frequency of the flights and $\langle x^2 \rangle$ is the mean square of the total distance of these flights. Now the components of eq. (12) should be found. For the mean square distances of the flights for each kind of particle we have:

$$\langle x_1^2 \rangle = \frac{2m_1^2 E^2}{k_1^2 [B]^2} \quad (13)$$

$$\langle x_2^2 \rangle = \frac{2m_2^2 E^2}{k_2^2} . \quad (14)$$

It is mentioned [2, 5] that the mean square of the total distance $\langle x^2 \rangle$ is not actually equal to the sum $\langle x_1^2 \rangle + \langle x_2^2 \rangle$ due to the dependency between forward and backward reactions. A study of this problem [ibid.] leads to the conclusion that the correct result is twice reduced sum of $\langle x_1^2 \rangle$ and $\langle x_2^2 \rangle$. Hence we obtain:

$$\langle x^2 \rangle = \frac{2E^2(u_1 - u_2)^2}{(k_1[B] + k_2)^2} . \quad (15)$$

The mean frequency of the flights, n , is the inverse of the average lifetime $\langle \tau \rangle$. It can be evaluated from (7) as follows:

$$\langle \tau_1 \rangle = \frac{1}{[A_1]} \int_0^\infty t_1 k_1 [A_1] [B] \exp(-k_1 [B] t_1) dt_1 \quad (16)$$

$$\langle \tau_1 \rangle = \frac{1}{k_1 [B]}$$

$$\langle \tau_2 \rangle = \frac{1}{[A_2]} \int_0^\infty t_2 k_2 [A_2] \exp(-k_2 t_2) dt_2 \quad (17)$$

$$\langle \tau_2 \rangle = \frac{1}{k_2}$$

and

$$\langle \tau \rangle = \langle \tau_1 \rangle + \langle \tau_2 \rangle = \frac{k_1 [B] + k_2}{k_1 k_2 [B]}, \quad (18)$$

where $\langle \tau_1 \rangle$ and $\langle \tau_2 \rangle$ are the average lifetimes for the particles of each kind. Hence:

$$n = \frac{1}{\langle \tau \rangle} = \frac{k_1 k_2 [B]}{k_1 [B] + k_2} . \quad (19)$$

Finally, for the electrodiffusion coefficient we obtain:

$$D_e = \frac{E^2 k_1 k_2 [B] (u_1 - u_2)^2}{(k_1 [B] + k_2)^3} . \quad (20)$$

The second relationship between k_1 and k_2 of a one-stage reaction is given by the stability constant β :

$$\beta = \frac{k_1}{k_2} . \quad (21)$$

Equation (20) expresses the fact that the electrodiffusion effect increase with:

- decreasing reaction rates;
- increasing electric field gradient;
- increasing difference in the ion mobilities.

Combining eq. (17) and (21) the reaction rate constants k_1 and k_2 can be calculated. The great advantage of using horizontal zone electrophoresis is that methods for determining electromigration mobilities, diffusion coefficients and equilibrium constants are already developed.

Experiment

The no-carrier-added radionuclide used in electrophoretic experiments- ^{175}Hf ($T_{1/2}=70$ d, $E_\gamma=89.4$ keV (2.4 %), 343.4 keV (84 %), 433.0 keV (1.4 %)), was produced via $^{175}\text{Yb}(\alpha, n)^{175}\text{Hf}$ reactions on the U-200 cyclotron (FLNR, JINR). Its radiochemical purification was performed using ion-exchange chromatography [11]. The obtained $\text{Hf}(\text{NO}_3)_4$ had high specific activity. In each experiment a volume of 5 μl (100 kBq) of ^{175}Hf was injected into the electromigration cell. The average volume of the formed electrophoretic zone was approximately 150 μl , which corresponds to a hafnium concentration of $10^{-10} - 10^{-11}$ M.

An electric field gradient of $10 \text{ V}\cdot\text{cm}^{-1}$ was applied in the electrophoretic runs. Under the influence of the constant electric field, ions are forced to the electrode of opposite charge. The migration of the formed radioactive zone was observed by continuously scanning the electrophoretic tube with a $\text{CsI}(\text{Tl})$ detector of the completely automated electrophoretic device. In the diffusion experiment the expansion of the active zone was tracked during a period of 12 h by periodically scanning the electromigration tube.

In order to avoid hydrodynamic fluxes, the connection between the electrode cells and the electromigration tube was realized by means of a nucleopore filter ($\phi=100$ nm). The electrolyte in the electrode cells was continuously refreshed by a peristaltic pump to counteract any influence of the electrolytic processes.

Temperature of the electrophoretic tube was set at 298.15 K with an accuracy of 0.05 K. The ionic strength of the electrolyte was adjusted by adding potassium nitrate. The necessary value of pH was obtained by adding the appropriate volumes of HNO_3 .

(Suprapur, Merck), and in each measurement it was controlled with a digital pH-meter with a precision of 0.05 pH. All the solutions used were prepared with *aqua bidestillata*.

Results and discussion

The experimental cycle of measuring chemical reaction rates must include four steps:

- Determination of the electrophoretic mobilities of the presented forms;
- Determination of the stability constant of the complex;
- Measurement of the experimental diffusion coefficient D_{exp} in the presence of a constant electric field with a gradient E ;
- Determination of the ordinary diffusion coefficient D in the absence of an external electric field.

Polyaminocarboxylic acid chelating agents like diethylenetriaminepentaacetic acid (DTPA) always interact with tetravalent cations in the ratio 1:1 and the charge of the complex is determined by the charge of the initial metal ion and the completely deprotonated ligand [12]. In the presence of DTPA following equilibrium takes place:

In a fast kinetics case, the mobility of the single formed zone is given by [10]:

$$\bar{u} = \frac{u_1 + u_2 [L] \beta}{1 + [L] \beta} \quad (23)$$

where:

$\bar{u}$ is the electrophoretic mobility of the zone;

u_1 is the mobility of the cation;

u_2 is the mobility of the complex;

$[L]$ is the ligand equilibrium concentration;

β is the complex stability constant;

Determination of the stability constant for $[\text{HfDTPA}]^-$ is described elsewhere [13], and the value $\log \beta = 28.72$ was obtained.

In order to determine the mobilities of the species, a cycle of electromigration experiments were performed. In 1 M HNO_3 at 298.15 ± 0.05 K and an electric field gradient $9.62 \text{ V} \cdot \text{cm}^{-1}$ the Hf(IV) cation mobility was found:

$$u_1 = (3.72 \pm 0.07) \cdot 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}.$$

To determine the electrophoretic mobility of the $[\text{HfDTPA}]^-$ complex form, electromigration runs were carried out under the following conditions:

electric field gradient $10 \text{ V} \cdot \text{cm}^{-1}$;

analytical concentration of DTPA $1 \cdot 10^{-5} \text{ M}$;

ionic strength $I = 0.10$;

$pH = 1.07$;
temperature $T = 298.15 \pm 0.05$ K.

Fig. 1. Position– time dependence, obtained in a migration experiment with $[HfDTPA]^-$. $\bar{u} = (-1.91 \pm 0.03) \cdot 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$.

After processing the experimental results in accordance with (23), the electromigration mobility of the complex form was determined:

$$u_2 = (-2.14 \pm 0.10) \cdot 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}.$$

In the course of measuring the ordinary diffusion coefficient of $[HfDTPA]^-$ a volume of $5 \mu\text{l}$ (100 kBq) of ^{175}Hf containing solution was injected into the electrophoresis tube and high voltage was applied. The formed active zone moved from the injection point to the homogeneous part of the electromigration tube under a constant electric field gradient of $10 \text{ V} \cdot \text{cm}^{-1}$. Then the high voltage was switched off and the scanning procedure started. The formed active zone is described by the Gaussian distribution function with the standard deviation:

$$(\sigma(t))^2 = 2Dt. \quad (24)$$

The scanning of the zone distribution profiles at different moments $t_1, t_2, \dots, t_n$ and determination of respective standard deviations $\sigma_1, \sigma_2, \dots, \sigma_n$ made it possible to linearly fit the function $\sigma^2 = f(t)$ and to calculate the diffusion coefficient of the Hf-DTPA complex

$$D = 7.76 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}.$$

The electrodiffusion coefficient was measured by continuously scanning the electrophoretic cell during the migration of the zone under the electric field gradient $E = 12.58 \text{ V} \cdot \text{cm}^{-1}$ under the experimental conditions listed below:

analytical concentration of DTPA $1 \cdot 10^{-5} \text{ M}$;
ionic strength $I = 0.10$;

$pH = 1.07$;

temperature $T = 298.15 \pm 0.05$ K;

The obtained dependence *standard deviation- time from start* is given in Table 1.

Table 1. Standard deviation of the zone as a function of time from start of the migration experiment

Time from start, s	Standard deviation of the zone, cm
552	0.36
1227	0.39
1404	0.39
1630	0.42
2010	0.44
2235	0.44
2400	0.46
2620	0.48
2826	0.49
3460	0.54

The electrodiffusion coefficient D_e is a measure of an extra expansion of a zone of two species that are in chemical equilibrium in an external d.c. electric field. As was mentioned above, ordinary diffusion, governed by the ordinary diffusion coefficient D , will be present in any experiment. If in an experiment with the presence of an electric field the measured diffusion coefficient is $D_{exp.}$, the electrodiffusion coefficient is given by the following equation:

$$D_e = D_{exp.} - D. \quad (25)$$

Taking into account the experimental data, presented in Table 1, the $[HfDTPA]^-$ electrodiffusion coefficient

$$D_e = 1.92 \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$$

was obtained.

Finally, in accordance with (20) the reaction rate constants were calculated:

$$\log k_1 = 26.46$$

$$\log k_2 = -2.29.$$

Conclusion

A method of measuring chemical reaction rates was developed. A scheme for investigation of complex formation and hydrolysis type chemical equilibrium was created. The relation between the electrodiffusion effect and equilibrium kinetic characteristics such as the reaction rate constants was shown. Thus, the possibilities for measuring the stability and hydrolysis constant was outlined.

The kinetic constants for DTPA complexation of $^{175}\text{Hf(IV)}$ were determined in a cycle of electrophoretic experiments, keeping the temperature and ionic strength constant.

The applying of horizontal zone electrophoresis in a free electrolyte has some advantages in investigation of reaction kinetics:

- chemical equilibrium is studied in its actual and undisturbed state;
- already developed techniques are used for measuring equilibrium constants and diffusion coefficients;
- the entire cycle of experiments is done on a single device;
- micro- and ultramicroconcentrations of isotopes are used;
- A wide set of additional parameters can be obtained during analysis.

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Божиков Г. А. и др.

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Исследование химических кинетических равновесий
электромиграционным методом

Разработан способ определения скоростных констант быстрых ионных реакций электромиграционным методом. Рассмотрена корреляция кинетики химических равновесий и электродиффузионных процессов при постоянном градиенте электрического поля. В модельном электрофоретическом эксперименте исследована кинетика комплексообразования Hf(IV) с диэтилен-триаминпентауксусной кислотой (ДТПА).

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Bozhikov G. A. et al.

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Investigation of Chemical Equilibrium Kinetics
by the Electromigration Method

Measurement of the chemical reaction rates for complex formation as well as hydrolysis type reactions by the method of horizontal zone electrophoresis is outlined. The correlation between chemical equilibrium kinetics and electrodiffusion processes in a constant d.c. electric field is described. In model electromigration experiments the reaction rate constant of the complex formation of Hf(IV) and DTPA is determined.

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

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