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**DETERMINATION OF ION MOBILITIES
OF RADIONUCLIDES
IN A FREE ELECTROLYTE.**

Methods and Experimental Organization

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One of the methods of studying physical and chemical properties of ions and aqueous solutions is based on the determination of their mobilities in a homogeneous electric field. The method allows to judge oxidizing states of ions, about production of associates and complex compounds, to determine their stability constants, to investigate kinetics of some reactions^{1/}. The method avoids undesirable, in some cases, reactions requiring introduction of heterogeneous phases, e.g., ion-exchange resin or extragents. It is suitable for investigation of ultramicroquantities of synthetic elements, astatine in part. Astatine, the last element in the halogenic group, has the most long-lived isotopes of less than 10-hour half-life. Iodine is practically excluded as a non-isotopic carrier due to more electropositive character of astatine, classified with half-metals. Therefore astatine microquantities are liable to interactions with non-controllable admixtures which are possible in a system with the heterogeneous phase. This results in cases where side reactions make interpretation of experimental data far too complicated or just impossible. Obviously, astatine is the most suitable element for investigation of its properties through the measurement of its ion mobilities in an electric field.

In infinitely diluted solutions with no interior interactions the mobility becomes a characteristic value of an ion, affected by ion-solvent interactions only. The limiting mobilities of ions are usually determined by extrapolation to zero concentration taking into consideration the values of mobilities in final concentrations of electrolytes. In order to calculate concentration mobilities of ions the data on equivalent electric conductivity and transfer numbers found with the error of order of 0.1 per cent are mostly used. It is obvious that this procedure is not good for astatine or other elements available in ultramicroquantities only. A well-practiced technique of zone electrophoresis on porous carriers is also out of question because of the necessity to introduce a number of empiric coefficients and because of unavoidable adsorption of microelements on developed surfaces, what reduces the accuracy and reproducibility of determinations.

Tentative experiments on determination of ion migration rates by horizontal zone electrophoresis in free electrolytes showed the possibility of getting reproducible results^{2/}. This has become the basis for new better technique of determination of ion

electromigration rates in free electrolytes. This paper deals with the description of the facility, organization of the experiment and discussion of some experimental details. The technique has been thoroughly tested with the iodide anion and the terbium cation.

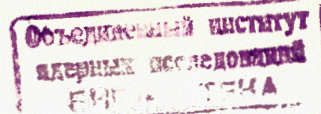
THE MEASURING CELL

The glass measuring cell for determination of ion electrophoretic mobilities is shown in Fig.1a. Ions migrated in a horizontal tube (7), 500 mm long, 4 mm in diameter. The tube had three vertical open branch pipes. Through one of them (3) the solution of the investigated element was injected. The second (4) was used to measure voltage gradient, and the third one (5) - to slip in the temperature control gauge. High voltage (up to 1000 V) was fed into platinum electrodes (1) covered with protecting glass cylinders (2) and slid in electrolyte vessels. The tube (7) and the vessels (8) had a glass thermostate casing. TYP 2000/0.1 stabilizer, produced by Statron, DDR, was used as the high voltage supply source. Voltage gradient in the migration tube was measured with the V530 high-resistance digital voltmeter, produced by Mera-Tronik, Poland.

THE RADIATION DETECTOR

Distribution of radioactive ions in the electromigration tube was measured by a scintillation detector with NaI(Tl) crystal (ϕ 12 mm, h = 30 mm, energy resolution - 10%). The detector was covered with a lead shield and placed on a trolley (10 - Fig.1b), which moved all the time along the tube with a constant speed. A reversing electric motor with the worm gear was used to move the trolley.

In order to register only γ -quanta perpendicular to the scintillator plane a collimating slot 3-5 mm wide was made with two 10-mm mobile lead plates. It was enough to absorb 70-150 keV mild γ -radiation which was effectively registered by detectors with NaI(Tl) crystals of small volume. A thicker collimator did not reduce the background produced by Compton radiation and hard γ -quanta with regard to the measured effect. The effect-to-background ratio was, at best, constant. It increased essentially only when we cut in a 4096-channel ICA-70 amplitude analyser (KFKI, Budapest, Hungary), operating in multiskeller regime. The analyzer allowed to detect γ -quanta within the prescribed energy range at the strictly determined exposure. The pulses registered at each scanning step were recorded consequently in memory cells of the analyser. The block-diagram of the facility is shown in Fig.1b.



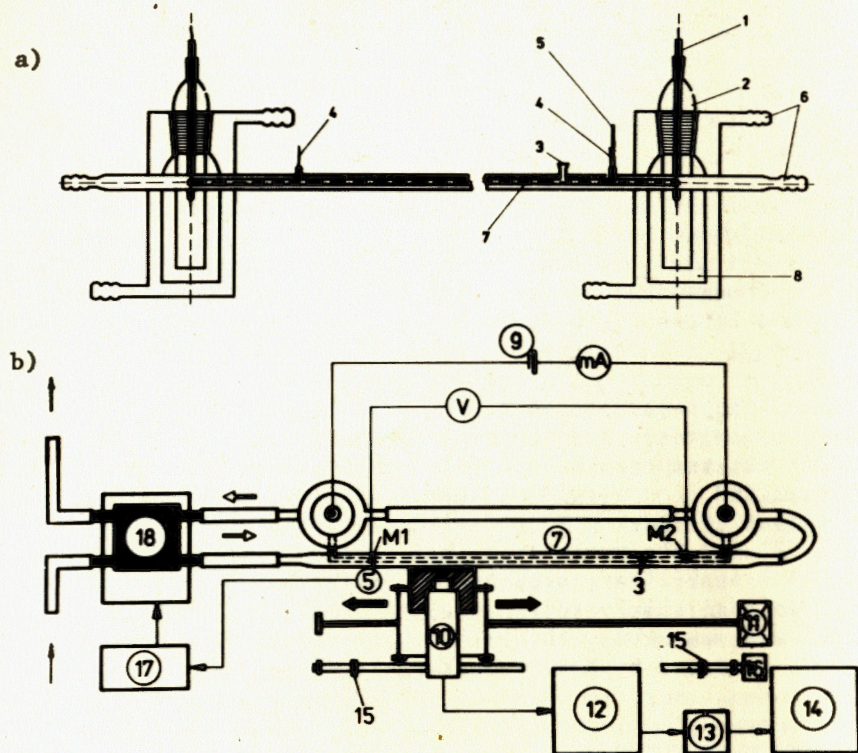


Fig. 1. The facility for electrophoresis in free solutions. a) the glass cell, b) the facility block-diagram. 1 - platinum electrodes; 2 - ground-in cylinders; 3 - activity inlet; 4 - voltage measuring electrodes; 5 - temperature gauge; 6 - thermostat casing; 7 - electromigration tube; 8 - electrolyte vessels; 9 - high voltage supply source; 10 - radiation detector; 11 - reversing electric motor; 12 - MAA ICA-70; 13 - master crate with interfaces; 14 - EC-1010 computer; 15 - mobile limiters; 16 - switch for changing direction of movement; 17 - thermostat temperature regulating unit; 18 - thermostat.

STABILIZATION OF ELECTROLYTE TEMPERATURE

In order to get reproducible values of mobilities ion migration rates must be measured under standard temperature conditions. 1°C shift in temperature leads to relative errors $\sim 2\%$. A higher than in thermostat temperature in the electromigration tube due to Joule effect may be the source of the errors.

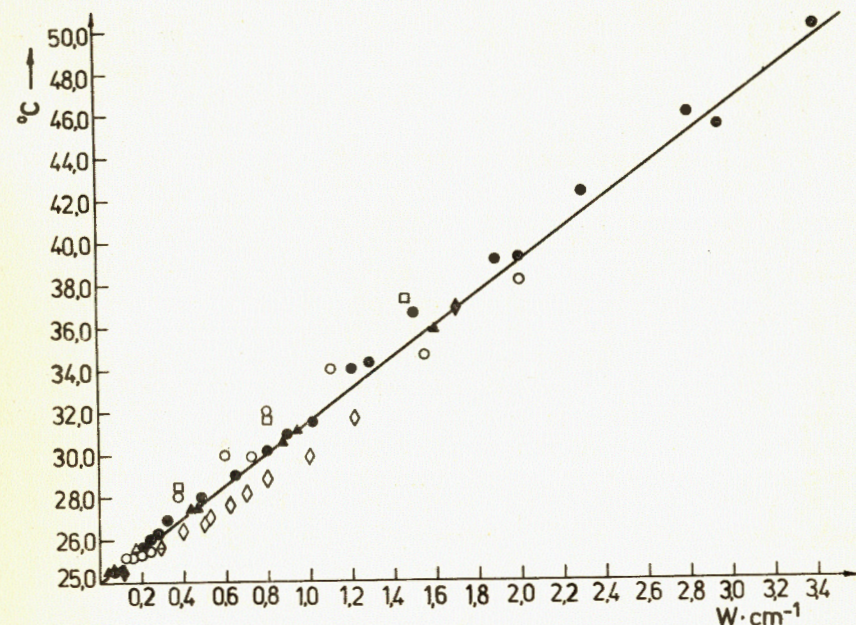


Fig. 2. Dependence of electrolyte temperature in the migration tube versus specific heat release at constant thermostat water temperature $25 \pm 0.1^{\circ}\text{C}$.

Measurements of the solution temperature in the tube by means of a silicon diode showed that it was equal to the temperature of the thermostat water only at very low heat release ($w \leq 0.015 \text{ Wt/cm}$). The temperature grew considerably as w increased (Fig. 2).

For temperature stabilization the temperature control gauge inside the tube and the thermostat were connected with a measure-and-control unit which always regulated the thermostat temperature in such a way that the electrolyte temperature in the tube was always constant within $\pm 0.1^{\circ}\text{C}$.

ORGANIZATION OF THE EXPERIMENT

The instruments for determination of ion mobility in free electrolytes are a part of the three-level system for acquisition, processing and analysis of spectrometric information developed in the Laboratory of Nuclear Problems, JINR^{3/}. These instruments are the lowest level of the system (Fig. 3). Communication between the CAMAC master crate and the EC-1010 computer of the second level was established by means of the KK004 gene-

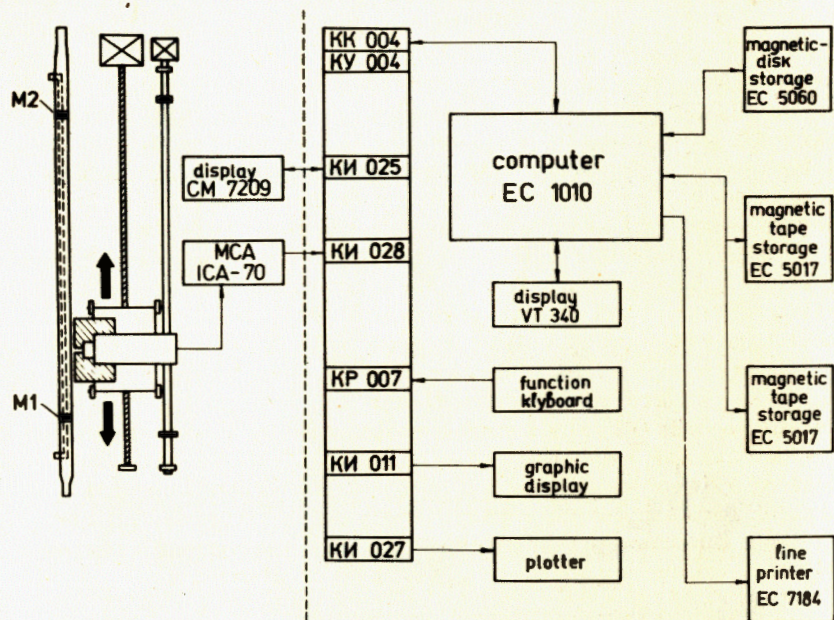


Fig.3. Schematic drawing of the experimental organization.

ral-purpose controller and the KU004 grader^{4,5/}. The EC-1010 computer was connected through the master crate with the ICA-70 multichannel analyser, functional keyboard, oscillographic display, plotter, CM 7209 remote display. Communication was established by means of KI 028, KP 007, KB 006, KI 027 and KI 025 interfaces^{6,7,8/}. VT 340 panel display or CM 7209 remote display were used to control the information transfer. With the help of these displays we filled in an identifier of 72 decimal digits which characterized the experimental conditions.

The identifier allowed to find rapidly tape-recorded results of the proper experiment and re-record them on the disk.

DETERMINATION OF ION CONCENTRATION MOBILITY

Determination of ion concentration mobility practically boils down to an accurate determination of the active zone movement rate at constant temperature and constant voltage gradient E (V/cm):

$$U_e = \Delta X / (E \Delta t), \quad (1)$$

where: ΔX is the covered distance (cm); Δt is the time (sec).

During continuous scanning of the tube the speed of detector movement was much higher than the active zone movement rate. This being the case, one could consider the zone to be in a quasistationary state. At the beginning of the experiment the activity distribution in the zone in the first approximation could be depicted by the symmetric Gaussian which gradually changes into an asymmetric form as electrophoresis goes on. Because of zone indistinctness a wide region of close-to-maximum activity is not a rare phenomenon. This makes it difficult to determine accurately the point of maximum. Therefore we used the shift of the zone gravity centre to determine the rate of movement. In order to locate the zone more accurately two radioactive point markers (M1 and M2 - Fig.3) were glued in the tube casing. They marked the section where the detector moved with a constant speed (V). One of these markers (M1) was employed as the coordinate origin with regard to which the time shift of the zone gravity centre was determined. Excerpts from information recordings of an experiment are given in Fig.4. At the measurement duration (τ) corresponding to one channel the distance (X_i) between the zone gravity centre and M1 is

$$X_i = (K_{ci} - K_{M1i}) V \tau.$$

where K_{ci} and K_{M1i} are numbers of the channels with gravity centres of active zones of the investigated ion and M1 at the i -th scanning series. Section boundaries were scanned and marked on the screen of the oscillographic display with the help of the functional keyboard. Gravity centres of zones and markers were determined by the moments method. The time after the beginning of the experiment, when the zone gravity centre was located, is $t_i = K_{ci} \tau$. Through 8-20 experimental points in the coordinate

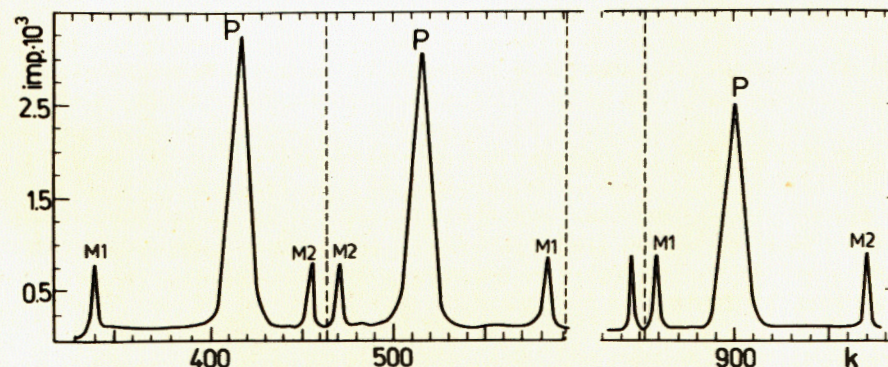


Fig.4. Excerpt from the analyser memory recordings of the intensity dependence versus the channel number. The zone with $^{131}\text{I}^-$ moves from M2 to M1.

system $X = f(t)$ a straight line was drawn according to the least squares method, and linear equation (2) parameters and their dispersions were estimated by formulae (3-6) /9/

$$X = \bar{X}^{\circ} + \bar{W}t, \quad (2)$$

where \bar{X}° is a constant equal in value to the distance between activity inlet and MI; X is a distance between MI and zone gravity centre t sec after the migration started; \bar{W} is the zone movement rate.

$$\bar{W} = (n \sum t_i X_i - \sum t_i \sum X_i) [n \sum t_i^2 - (\sum t_i)^2]^{-1}, \quad (3)$$

$$\bar{X}^{\circ} = (\sum t_i^2 \sum X_i^2 - \sum t_i X_i \sum t_i) [n \sum t_i^2 - (\sum t_i)^2]^{-1}, \quad (4)$$

$$S_{\bar{W}}^2 = S^2 [n \sum t_i^2 - (\sum t_i)^2]^{-1}, \quad (5)$$

$$S_{\bar{X}^{\circ}}^2 = S^2 \left[\frac{1}{n} + \frac{(\frac{1}{n} \sum t_i)^2}{n \sum t_i^2 - (\sum t_i)^2} \right], \quad (6)$$

where: $S^2 = [\sum (X_i - \bar{X}^{\circ} - \bar{W}t_i)^2] / (n - 2)$, n is a number of experimental points; $\sum = \sum_{i=1}^n$.

DETERMINATION OF THE MEAN CONCENTRATION MOBILITY VALUE

The repeated determinations (m) of ion mobility values at the prescribed concentration of the electrolyte numbered, as a rule, from 6 to 12. They differed, more or less, in values \bar{X}_j° and \bar{W}_j (where $j = 1$ before m). From the experimentally obtained values of \bar{X}_j with allowance for the statistical weight of a separate determination $P_j = 1/S_{\bar{X}_j^{\circ}}^2$ the value \bar{X}° and its dispersion were determined:

$$\bar{X}^{\circ} = (\sum P_j \bar{X}_j^{\circ}) [m \sum P_j]^{-1}, \quad (7)$$

$$S_{\bar{X}^{\circ}}^2 = (\sum P_j (\bar{X}_j^{\circ} - \bar{X}^{\circ})^2) [(m-1) \sum P_j]^{-1}. \quad (8)$$

We have mentioned above that the true value of X_0° was known. It has allowed to determine both statistical and non-statistical (systematic) errors by means of eq. (9)

$$|X_0^{\circ} - \bar{X}^{\circ}| < t_{pk} \sqrt{S_{\bar{X}^{\circ}}^2}. \quad (9)$$

where: t_{pk} is the Student coefficient at $p = 0.95$ and k degrees of freedom.

If requirement (9) was not satisfied, we excluded one by one from eq. (7) those \bar{X}_j° (though not more than 30 per cent from the initial) for which the difference $|\bar{X}^{\circ} - \bar{X}_j^{\circ}|$ was maximal. If in this case (9) was not yet satisfied, it indicated that these were systematic errors due to processes in the electromigration tube. The results of such experiments were not considered.

From all \bar{W}_j for which the corresponding \bar{X}_j° met requirement (9) the mean rate of the zone movement \bar{W} and its dispersion $S_{\bar{W}}^2$ were determined by formulae similar to (7) and (8).

DETERMINATION OF LIMITING IONIC MOBILITIES

It has been mentioned above that in infinitely diluted electrolytes ion mobility was affected only by interactions with solvent molecules, and absolute mobilities can be estimated by extrapolation of concentration mobilities, obtained at the concentration ($10^{-5} - 10^{-2}$ M), to the zero concentration of the electrolyte. On determining the limiting mobilities of microconcentrations of Γ^{-} and Tb^{3+} ions, we have employed a similar technique. Inasmuch as mean errors on determining U_c ranged from 0.5 to 2.0 per cent, depending upon the concentration of the background electrolyte, and exceeded considerably the mobility errors obtained through the measurement of electric conductivity, we confined ourselves to the linear extrapolation of the equation /10/ for the determination of

$$U_c = U_0 - k \sqrt{c}.$$

The values of U_c for iodide obtained with the help of $^{131}I^{-}$ are very close to the known data /11,12/ (fig.5). They grew with the degree of electrolyte dilution and give $U_c = 8.15 \pm 0.20 \cdot 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (25°C) at the extrapolation for infinite dilution. We failed, however, to find in references the mobility values or equivalent ion conductivity for terbium. On the basis of regular changes of ion mobilities of other lanthanides, depending upon their crystallographic ion radii, U_0 for Tb^{3+} must be $6.82 \cdot 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (25°C). According to our measurements (Fig.5) $U_0 = (7.00 \pm 0.15) \cdot 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

The U_0 obtained by us differed from the compared by less than 3 per cent (Fig.5). It is quite possible that we will be able to apply our technique to determination of limiting mobilities of astatine ions with the same accuracy.

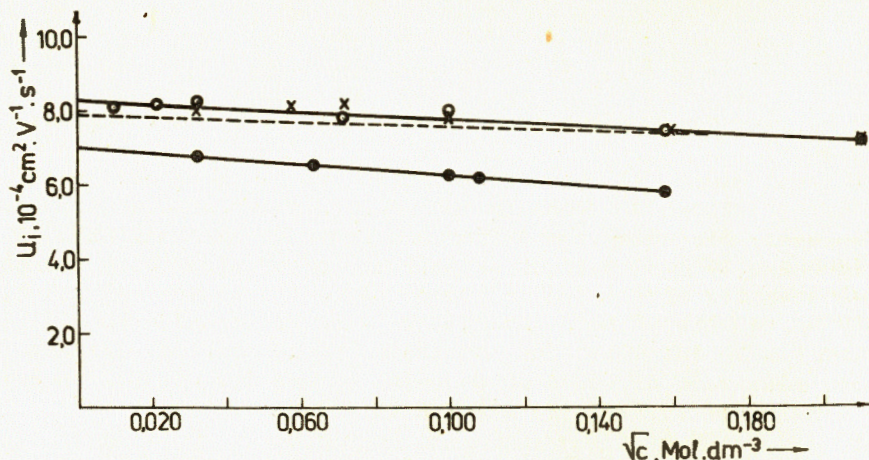


Fig.5. Mobilities of $^{131}\text{I}^-$ in NaOH and $^{160}\text{Tb}^{3+}$ in HClO_4 as functions of solution concentration at 25°C.
 — o — o — $^{131}\text{I}^-$ without carrier; — x — x — $\text{CsI}(^{131}\text{I}) 1 \cdot 10^{-4}\text{M}$;
 - - - - data from paper /12/; —●—●— $^{160}\text{Tb}^{3+}$.

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Определение подвижностей ионов радионуклидов
 в свободном электролите.

Методика и организация эксперимента

Разработан и проверен новый вариант метода измерения скоростей ионов с помощью горизонтального зонного электрофореза в свободных растворах. Приводится схема установки, обсуждаются некоторые детали эксперимента и результаты измерений предельных подвижностей $^{131}\text{I}^-$ и $^{160}\text{Tb}^{3+}$, на примере которых проверялась воспроизводимость метода.

Работа выполнена в Лаборатории ядерных проблем ОИЯИ.

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