

Electromigration of Carrier-Free Radionuclides.

6. Iodide and Bromide Complexes of Carrier-Free $^{201}\text{Tl(I)}$ in Aqueous Solutions

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Dedicated to Academician G. N. Flerov on the Occasion of his 75th Birthday

Individual ion mobility of $^{201}\text{Tl(I)}$ $u_{\text{Tl}^+}^0 = +7.3(3) \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ was observed at $298.1 \pm 0.1 \text{ K}$ in aqueous solutions of H(K)ClO_4 , $1.5 \cdot 10^{-3} \leq \mu \leq 0.5$ and $0.3 \leq \text{pH} \leq 6.5$. Experimental dependences of $^{201}\text{Tl(I)}$ overall ion mobilities on concentrations of ligand anions in solutions of perchlorate background electrolytes have been used to calculate stability constants of neutral thallium complexes TlI and TlBr at $298.1 \pm 0.1 \text{ K}$ and $\mu = 0.1$. They are $115 \pm 25 \text{ l} \cdot \text{mol}^{-1}$, and $5.25 \pm 0.35 \text{ l} \cdot \text{mol}^{-1}$ respectively.

In wäßrigen H(K)ClO_4 -Lösungen von $T = 298,1 \pm 0,1 \text{ K}$, $1,5 \cdot 10^{-3} \leq \mu \leq 0,5$; $0,3 \leq \text{pH} \leq 6,5$, wurden individuelle Ionenbeweglichkeiten des Tl(I) von $u_{\text{Tl}^+}^0 = +7,3 \pm 0,3 \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ gemessen. Aus den experimentellen Abhängigkeiten der Tl(I) -Bruttoionenbeweglichkeit von den Konzentrationen der anionischen Liganden sind die Stabilitätskonstanten der neutralen Komplexverbindungen TlI und TlBr bei $T = 298,1 \pm 0,1 \text{ K}$ und $\mu = 0,1$ berechnet worden. Sie betragen $115 \pm 25 \text{ l} \cdot \text{mol}^{-1}$ bzw. $5,25 \pm 0,35 \text{ l} \cdot \text{mol}^{-1}$.

Keywords

electrophoresis; ion mobility; thallium 201; thallium bromides; thallium iodides

1. Introduction

Complexes of thallium(I) with halides or other single-charged ligands were earlier studied by various groups of authors [1–9]. They found mononuclear complexes with $n = 1–4$ ligands, and even up to six ligands for iodide associates.

In many papers difficultly soluble salts of Tl(I) were investigated. Dependence of their solubility on concentration of ligand anions in solutions with variable and constant high overall ionic strength μ was determined. Using solubility curves, one could calculate composition and stability of complexes formed under these conditions if one makes some assumptions, e.g. on changes in ion activities and on solubility products of thallium(I) salts in concentrated solutions of electrolytes of varying composition. Using solubility methods in bromide and iodide systems give rise to additional difficulties in experiments due to the extremely low concentrations ($10^{-5} \dots 10^{-7} \text{ M}$) of Tl(I) in solutions. Regions, where mainly neutral and single-charged anionic complexes exist, coincide with minima in curves of Tl(I) bromide and iodide solubilities in solutions with like ligand anions. Therefore we think that it is more suitable to determine complex formation constants of thallium(I) complexes by a radically different method, i.e. by measuring Tl(I) overall ion mobility in diluted solutions of inert background electrolytes at a constant overall ionic strength and with varying concentrations of ligand anions. We have modified the method of horizontal zone electrophoresis [10–12], and now our version allows directly measuring migration mobilities of microquantities of radioactive elements and calculating individual ion mobilities, metal ion hydrolysis and complex formation constants on the basis of experimental data [13–16].

This paper deals with determination of stability constants of neutral associates TlBr and TlI . Experiments were carried out with carrier-free radiothallium ^{201}Tl .

2. Experimental

The ^{201}Tl sample was acquired in the "Isotope" office; it contained quite large amounts of NaCl . Thallium was separated from them by sorption in a Dowex 50×8 cation-exchange column. Tl(I) was washed out by 1 M HCl , the solution was dried by evaporation, and radiothallium was solved in $1 \cdot 10^{-2} \text{ M HClO}_4 + 1 \cdot 10^{-3} \text{ M N}_2\text{H}_5^+$. This was the initial solution with specific volume activity of about $1 \text{ GBq} \cdot \text{ml}^{-1}$ for preparing working solutions of ^{201}Tl – thallium(I). The technique, order and equipment of the experiments (Figs. 1 and 2) were the same as in our previous papers [13–16]. Ion mobility of Tl(I) was measured at $\Delta E = 10.00(1) \text{ V} \cdot \text{cm}^{-1}$ and $T = 298.1(1) \text{ K}$ in solutions of the following electrolytes:

- (i) H(K)ClO_4 , $1.5 \cdot 10^{-3} \leq \mu \leq 0.50$; $0.3 \leq \text{pH} \leq 6.5$
- (ii) $9 \cdot 10^{-2} \text{ M} \leq \text{KI} \leq 1 \cdot 10^{-5} \text{ M} - \text{H(K)ClO}_4$, $\mu = 0.1$,
 $\text{pH } 1.3 \dots 2.0$
- (iii) $9 \cdot 10^{-2} \text{ M} \leq \text{KBr} \leq 1 \cdot 10^{-5} \text{ M} - \text{H(K)ClO}_4$, $\mu = 0.1$,
 $\text{pH } 1.3 \dots 2.0$.

To stabilise the thallium(I) cation, hydrazine of 10^{-4} M concentration was added to the solutions. To check influence of possible occasional effects, related to the use of carrier-free ^{201}Tl upon the results, in several experiments thallium concentrations in the background electrolytes were $1 \cdot 10^{-4} \text{ M}$ (adding of $\text{Tl(ClO}_4)_3$). Chemically pure and analytically pure agents and bidistilled water were used.

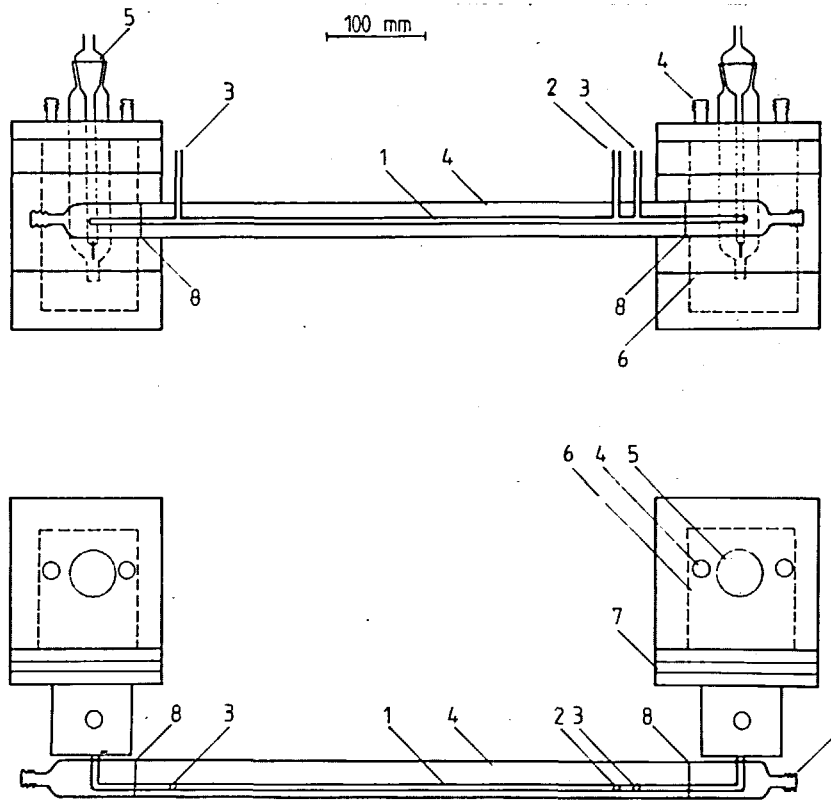


Fig. 1. Lay-out of the electromigration cell

1 - electromigration tube of glass, 2 - outlet to inject radionuclide solutions, 3 - outlets to insert a thermosensor and voltage measuring electrodes, 4 - tubes to supply water for thermostating, 5 - platinum electrodes, 6 - electrode chambers, 7 - flanges to fix hydrodynamic resistors, 8 - fixed radioactive mark

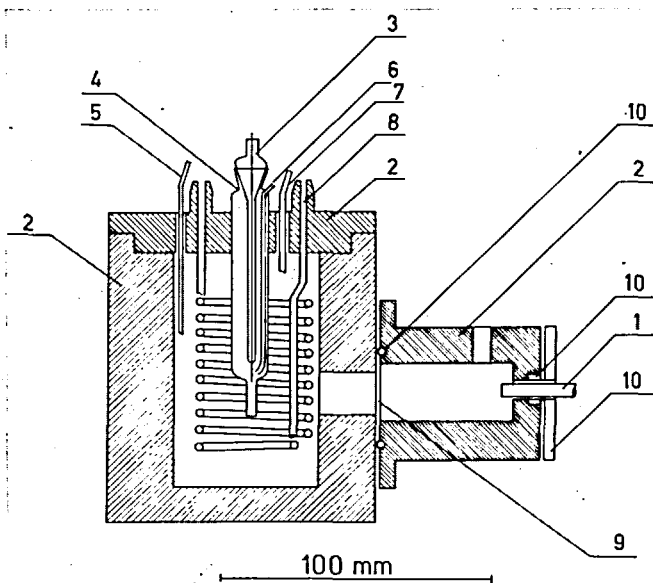


Fig. 2. Lay-out of the electrode chambers

1 - electromigration tube, 2 - plexiglass, 3 - platinum electrodes, 4 - glass vessels, 5 - outlet of electrolyte solution, 6 - inlet of electrolyte solution, 7 - outlet of electrolyte solution (overflow), 8 - thermostatic casing, 9 - hydrodynamic resistors (nuclepore filters), 10 - connecting links

3. Results and Discussion

Individual ion mobility u^0 of ^{201}Tl remained constant in solutions of inert electrolytes without bromide and iodide

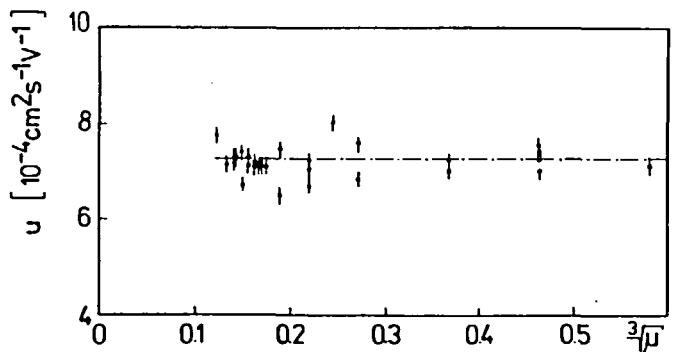


Fig. 3. $^{201}\text{Tl-Tl}^+$ individual ion mobility in $\text{H}(\text{K})\text{ClO}_4$ solutions versus overall ionic strength μ ; $T = 298.1$ (1) K, $0.3 \leq \text{pH} \leq 6.5$, (O) carrier-free $^{201}\text{Tl}(\text{I})$, (●) electrolytes containing $1 \cdot 10^{-4} \text{ M TlClO}_4$

when HClO_4 concentration changed by more than two orders - from $1.5 \cdot 10^{-3} \text{ M}$ to 0.50 M , when pH increased from 0.3 to 6.5 at $\mu = 0.1$, and when $1 \cdot 10^{-4} \text{ M}$ of thallium(I) was present in solutions with $\mu = 0.1$ and $\text{pH} 2$.

The results of these experiments are shown in Fig. 3. A mean value of ^{201}Tl -thallium(I) individual ion mobility was calculated on the basis of these data; it is regarded as the individual ion mobility of Tl^+ in perchloric acid solutions with $1.5 \cdot 10^{-3} \leq \mu \leq 0.50$ at 298.1 (1) K: $u_{\text{Tl}}^0 = +7.3(3) \cdot 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. It appeared to be close to the mobility of Tl^+ in infinitely diluted aqueous solutions ($\mu = 0$): $u_{\text{Tl}}^{\mu=0} = +7.75(15) \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$, calculated on the basis of reference data [17].

4. Neutral Complexes [TII] and [TIBr]

Results of experimental measurements of Tl(I) overall ion mobility ($\bar{u}_{\text{Tl(I)}}$) in solutions of electrolyte systems (ii, iii) at $\mu = 0.1$ with Br^- and I^- concentrations $< 0.1 \text{ M}$ are shown in Fig. 4. The character of dependences $\bar{u}_{\text{Tl(I)}} = f([\text{X}^-])$ allows an assumption that changes in overall ion mobilities $\bar{u}_{\text{Tl(I)}}$ are due to formation of the neutral complex compound [TIBr] in (ii) solutions ($[\text{Br}^-] < 0.1 \text{ M}$), and due to formation of [TII] and, probably, of $[\text{TII}_2]^-$ in iodide-containing solutions (iii).

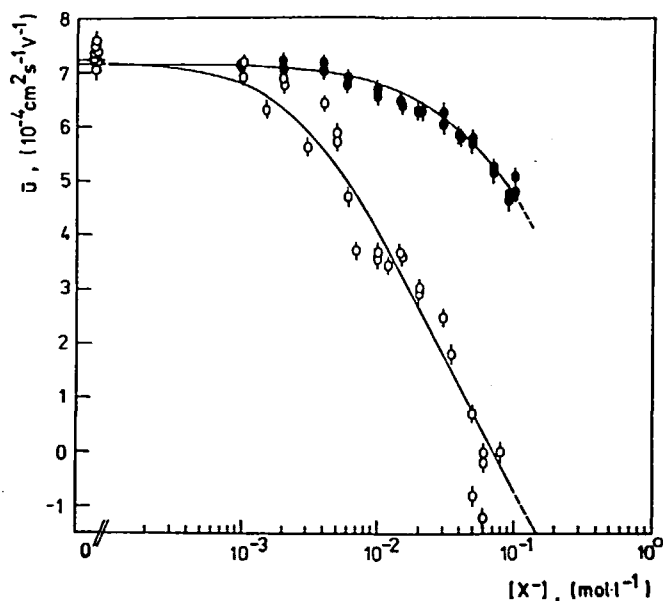


Fig. 4. ^{201}Tl -Tl(I) overall ion mobility in $\text{H}(\text{K})\text{ClO}_4$ solutions versus bromide (\bullet) and iodide (\circ) concentration; $T = 298.1$ (1) K, $p\text{H} 1.2 \dots 2.0$; solid lines are calculated curves

In the latter case the dependence of Tl(I) overall mobility upon the ligand anion concentration is described by equation (1):

$$\bar{u}_{\text{Tl(I)}} = \frac{u_{\text{Tl}^+}^0 + u_{[\text{TII}_2]^-}^0 \cdot \beta_2 [\text{I}^-]^2}{1 + \beta_1 [\text{I}^-] + \beta_2 [\text{I}^-]^2}, \quad (1)$$

where $u_{[\text{TII}_2]^-}^0$ is the individual ion mobility of the complex ion; β_1 and β_2 are the stoichiometric complex formation constants. Since measurements were carried out in solutions with relatively low amounts of $[\text{TII}_2]^-$, the value of $u_{[\text{TII}_2]^-}^0$ was taken to be $-7(2) \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ for solving the set of equations (1) by the least squares method with the use of the computer program MINUIT [18]. This value is based on the available data on approximately equal absolute values of single-charged oxalate complexes of trivalent metals [14, 15], of NpO_2^+ and $[\text{NpO}_2(\text{OH})_2]^-$ [16] and others. Other parameters — $u_{\text{Tl}^+}^0$, β_1 and β_2 — were regarded as independent. They were arbitrarily selected.

The numerical calculations yielded the stability constant β_1 of the thallium(I) iodide complex $\beta_1 = 115(25) \text{ l} \cdot \text{mol}^{-1}$. The second formation constant was determined with a large error ($\beta_2 = 400(250) \text{ l} \cdot \text{mol}^{-1}$). This results may only be used to estimate the order of magnitude of the formation constant. The calculated individual ion mobility of Tl^+ , $u_{\text{Tl}^+}^0 = +7.20(15) \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$, is in good agreement with the value determined in direct measurements. The curve calculated by equation (1) with the above mean values of constant parameters satisfactorily coincides with experimental points (Fig. 2).

In the case of bromide-containing systems, where the complex anion does not affect $\bar{u}_{\text{Tl(I)}}$, equation (1) is transformed into (2):

$$\bar{u}_{\text{Tl(I)}} = \frac{u_{\text{Tl}^+}^0}{1 + \beta_1 [\text{Br}^-]} \quad \text{or} \quad \beta_1 = \frac{u_{\text{Tl}^+}^0 - \bar{u}_{\text{Tl(I)}}}{\bar{u}_{\text{Tl(I)}} \cdot [\text{Br}^-]} \quad (2)$$

Solution of equation (2) yielded the value of the stability constant of the neutral complex [TIBr]; $\beta_1 = 5.25(35) \text{ l} \cdot \text{mol}^{-1}$.

It is difficult to compare the calculated stability constants of thallium(I) complexes with many available data, since the latter were obtained in solutions whose composition differed from those used to measure Tl(I) ion mobilities.

However, present values can be compared with complex formation constants calculated on the basis of thallium(I) bromide and iodide solubilities in solutions with growing overall ionic strengths: $0.01 \text{ M} < \text{KI} < 5.5 \text{ M}$, $\beta_1 = 74 - 28 \text{ l} \cdot \text{mol}^{-1}$ [2, 3] and $0.3 \text{ M} \ll \text{KBr} \ll 4.0 \text{ M}$, $\beta_1 = 5.4 - 3.8 \text{ l} \cdot \text{mol}^{-1}$ [4]. In the first case the value of the constant is three times smaller than ours. It seems to be wrong, since substituting this value and that of the second constant in equation (1) yields significantly higher calculated values of $\bar{u}_{\text{Tl(I)}}$ than experimental ones. The compared values for the thallium(I) bromide complex were close to one another. Noteworthy is that $\beta_1 = 5.35 \text{ l} \cdot \text{mol}^{-1}$ [4], determined in 0.5 M LiClO_4 , coincided with our calculated value.

Investigation of properties of traces concentrations of elements by electrophoresis is usually carried out in diluted ($\mu \approx 0.1 \dots 0.2$) solutions of background electrolytes. But the performed series of experiments allowed a conclusion that our experimental set-up permits in principle using even more concentrated solutions with overall strengths of the order of 1 M . Then measurements of carrier-free ^{201}Tl (I) ion mobility at higher concentrations of ligand anions make it also possible to determine complex formation constants not only for neutral, but also for thallium halide complexes with $n = 2, 3, \dots$ ligands. Additional, in this case values of individual ion mobilities of these complex anions obtained by mathematical processing of experimental data will be of special interest.

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Electromigration of Carrier-Free Radionuclides. 7. ^{201}Tl -Thallium(I) Sulphate Complexes in Aqueous Solutions

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Dedicated to Academician G. N. Flerov on the Occasion of his 75th Birthday

Stoichiometric stability constants of the thallium (I) sulphate complex $[\text{Tl}(\text{SO}_4)]^-$ have been determined by measurements of the ^{201}Tl - $\text{Tl}(\text{I})$ ion mobility at 298.1 (1) K in solutions of $\text{Na}_2\text{SO}_4/\text{Na}(\text{H})\text{ClO}_4$, $\mu = 0.1$, $\text{pH} \leq 4$, and $\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4$, $0.1 \leq \mu \leq 0.48$, $\text{pH} 2-2.5$. The thermodynamic stability constant of this complex anion of $K_1^0 = 15.7(1.0) \text{ l} \cdot \text{mol}^{-1}$ has been calculated on the basis of experimental data.

Durch Messungen der ^{201}Tl - $\text{Tl}(\text{I})$ -Ionenbeweglichkeit in Lösungen des Typs $\text{Na}_2\text{SO}_4/\text{Na}(\text{H})\text{ClO}_4$, $\mu = 0,1$, $\text{pH} \leq 4$, bzw. $\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4$, $0,1 \leq \mu \leq 0,48$, $\text{pH} 2-2,5$, sind stöchiometrische Stabilitätskonstanten des Thallium(I)-Sulfat-Komplexes $[\text{Tl}(\text{SO}_4)]^-$ bestimmt worden. Aus den experimentellen Daten sind thermodynamische Stabilitätskonstanten des Komplexanions zu $K_1^0 = 15,7 (1,0) \text{ l} \cdot \text{mol}^{-1}$, $T = 298,1 (1) \text{ K}$, berechnet worden.

Keywords

ion mobility; stability; thallium 201; thallium complexes; thallium sulfates; thermodynamic properties

1. Introduction

In our previous communication [1] one could find values of stoichiometric stability constants for bromide and iodide complexes of thallium(I) cation in dilute halide/perchlorate solutions with varying halide concentration and constant overall ionic strength μ . The constants were calculated on the basis of electromigration measurements of carrier-free radiothallium(I) ^{201}Tl in $\text{Na}(\text{H})\text{ClO}_4$ inert electrolytes. The electrophoretic method employed allowed well-reproducible experimental data exactly under those low overall ionic strength conditions when other methods yield relatively large errors for values of thallium(I) complex stability constants.

This paper continues investigations of monovalent thallium complexes. We have studied $\text{Tl}(\text{I})$ overall ion mobility $\bar{u}_{\text{Tl}(\text{I})}$ in sulphate containing solutions with overall ionic strengths μ less than 0.5. According to literature data, a thallium(I) sulphate anion $[\text{Tl}(\text{SO}_4)]^-$ is formed in these solutions [2–11]. The value of its thermodynamic stability constant K_1^0 is in the interval from 10 to $100 \text{ l} \cdot \text{mol}^{-1}$, according to the recent measurements [9]. Such a noticeable spread makes it desirable to carry out additional determinations of thermodynamic and stoichiometric stability constants of the thallium(I) sulphate complex, respectively.

2. Experimental

^{201}Tl : The carrier-free radionuclide ^{201}Tl acquired through the firm "Isotope" has been used for investigations. Prepa-

ration of the radiothallium sample for the experiments is described in ref. [1]. Radiothallium in stock solutions of $10^{-2} \text{ mol} \cdot \text{l}^{-1} \text{ HClO}_4/10^{-4} \text{ mol} \cdot \text{l}^{-1} \text{ N}_2\text{H}_4$ was injected into the migration cell. The injected volume was of about 1 to $3 \mu\text{l}$.

Electrolytes: The overall ion mobility of radiothallium ^{201}Tl - $\text{Tl}(\text{I})$ (migration rate at the voltage gradient $1 \text{ V} \cdot \text{cm}^{-1}$) was determined at the temperature 298.1(1) K in solutions of background electrolytes $\text{Na}(\text{H})\text{ClO}_4$ with constant or varying overall ionic strength μ : $\text{Na}_2\text{SO}_4/\text{Na}(\text{H})\text{ClO}_4$, $\mu = 0.1$, $\text{pH} \approx 4$, and $\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4$, $0.1 \leq \mu \leq 0.48$, $\text{pH} 2 \dots 2.5$. In all electrolytes the presence of $10^{-4} \text{ mol} \cdot \text{l}^{-1} \text{ N}_2\text{H}_4$ stabilised radiothallium in the monovalent oxidation state.

Concentrations of sulphate ions at the given acidities were calculated with allowance for variation of dissociation constant $K = [\text{SO}_4^{2-}] \cdot [\text{H}^+] \cdot [\text{HSO}_4^-]^{-1}$, inversely proportional to the overall ionic strength of the solutions [12, 13].

All electrolytes are prepared with chemically pure agents and bidistilled water immediately before the experiments.

Electromigration method: Direct measurements of radiothallium ion mobilities were performed by means of a set-up developed in our laboratory. It allows carrying out on line electrophoresis in electrolytes free of finely divided inert fillers, at constant voltage gradients, temperature and chemical composition of background solutions [14, 15].