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**ELECTROMIGRATION  
OF CARRIER-FREE RADIONUCLIDE IONS  
IN ELECTROLYTES.  
HYDROLYSIS OF Bi(III)  
IN AQUEOUS SOLUTION**

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## Introduction

Hydrolysis of Bi(III) cations has been investigated many times. It was shown that polymeric compounds like  $\text{Bi}_6(\text{OH})_{12}^{6+}$  or  $\text{Bi}_9(\text{OH})_x^{(27-x)+}$  are produced if the concentration of the element in solutions exceeds  $2 \cdot 10^{-4} \text{ M}$  /1-4/. If a solution contains a trace amount of bismuth, hydrolysis yields monomeric products  $\text{Bi}(\text{OH})_n^{3-n}$ , where  $n = 1, 2, 3, 4$  /5-11/. Their hydrolysis constants are given in Table 1.

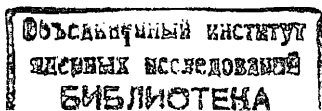
**Table 1.** Literature data of monomeric Bi(III) hydrolysis constants in electrolyte solutions

T(K)	$\mu(\text{M})$ , electrolyte	$\text{pK}_1$	$\text{pK}_2$	$\text{pK}_3$	$\text{p}\beta_3$	$\text{p}\beta_4$	Ref.
298.1	0.2 $\text{NaClO}_4$		1.9				/5/
298.1	3.0 $\text{NaClO}_4$	1.58					/6/
	$\text{HNO}_3$	2.0	3.37				/7/
298.1	0.1 $\text{NaClO}_4$	1.43			10.04	23.10	/8/
298.1	1.0 $\text{NaClO}_4$	1.55	2.82				/9/
295.1	0.1 $\text{KNO}_3$	1.55	1.97	2.42	5.94		/10/
"	0.3 "	1.50	1.95	2.48	5.93		/10/
"	0.5 "	1.41	1.85	2.32	5.58		/10/
"	1.0 "	1.34	1.76	2.19	5.29		/10/
288.1	1.0 $\text{NaClO}_4$		2.82				/11/
"	" "		3.20 ( $\text{D}_2\text{O}$ )				/11/

We have studied the equilibrium  $\text{Bi}^{3+} \rightleftharpoons \text{Bi}(\text{OH})_n^{3-n}$  by means of a method which was never used for this purpose before. This is a horizontal electrophoresis of carrier-free Bi(III) ions in aqueous electrolyte solutions with different pH. The experimental equipment and technique are considered in detail in the papers /12-14/.

## Experimental

Carrier-free samples of  $^{205}\text{Bi}$  ( $t_{1/2} = 15.3$  days, K-capture,  $\gamma$ ) and  $^{206}\text{Bi}$  ( $t_{1/2} = 6.24$  days, K-capture,  $\gamma$ ) radionuclides were used for the investigation. Radiobismuth was synthesized in reactions of



the (p, Xn) type at exposure of a lead target  $4 \text{ g}\cdot\text{cm}^{-2}$  thick to protons with the initial energy 65 MeV in the external beam of the isochronous cyclotron U-240 (INR of the Academy of Sciences of the Ukrainian SSR, Kiev).

The technique of radiobismuth separation, purification and concentration was based on its co-precipitation with ferric hydroxide and further ion-exchange in the column with anionite Dowex 1x8 /15/. The radionuclide purity was checked by gamma-spectra. Specific volume activity of the initial  $^{205}, ^{206}\text{Bi}$  stock-solution was about  $10 \text{ GBq}\cdot\text{ml}^{-1}$  in  $0.1 \text{ M HNO}_3$ .

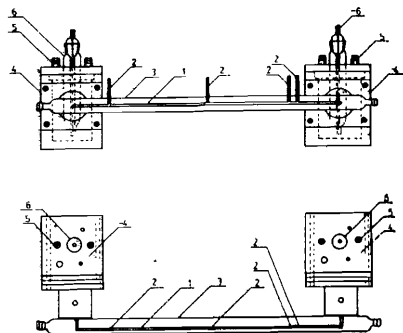


Fig. 1. Schematic view of the electromigration cell. 1 - electromigration tube of glass; 2 - pipes to put a temperature sensor, voltage-measuring electrodes and working solution into the tube; 3 - thermo-static casing; 4 - electrode chambers; 5 - unions to supply water for cooling the electrode chambers; 6 - platinum electrodes.

Migration mobilities of bismuth ions were measured at  $T=298.10$  (10)K in the following solutions:  $\text{Na(H)ClO}_4$ ,  $\mu = 0.25 \text{ M}$ ,  $0.75 \leq \text{pH} \leq 3.25$ ;  $\text{Na(OH)ClO}_4$ ,  $\mu = 0.25 \text{ M}$ ,  $12.6 \leq \text{pH} \leq 13.3$ ;  $0.4 \text{ M}$  and  $0.5 \text{ M NaOH}$ . The pH value of acid solution was measured by means of a glass electrode with the error  $\pm 0.05$ . The instrument operation was checked by standard buffer solutions produced by VEB Feinchemie Sebnitz, GDR. Each measurement was carried out with a fresh electrolyte made of bidistilled water and chemically pure agents. The solutions were poured into an electromigration cell (see Fig. 1). There the selected temperature of the solution was achieved thermostatically. Then 1-2  $\mu\text{l}$  of the initial bismuth solution were added to the contents of the electromigration tube. Continuous high voltage was applied to the electrodes; it produced a field with the linear gradient of  $10.0 \text{ V}\cdot\text{cm}^{-1}$  in the tube. The moving zone of radiobismuth was narrow for all pH and had a distinct maximum. The electromigration tube was continuously scanned by a scintillation detector with the  $\text{NaI(Tl)}$  crystal. This allowed a repeated determination of the maximum position and registration of the time of measurement during the experiment. The value of pH in the cell was the same during the experiment, the temperature conditions were maintained automatically with a special electric block /49/.

## Definitions and Symbols

"Electromigration" or "ion mobility" ( $u_i$ ) means here motion of ions in a constant electric field with the voltage gradient of  $1 \text{ V}\cdot\text{cm}^{-1}$ .

The motion "overall ion mobility" ( $\bar{u}$ ) is related to the mobility of a zone where the radioelement may be in several equilibrium forms.

The symbol  $u_i^0$  is for mobility of a specific ion at the given parameters of the electrolyte: overall ionic strength, temperature, chemical composition. If there is equilibrium between several ion forms of an element in the solution under those conditions, the quantity  $u_i^0$  shows the individual ion mobility of an ion  $i$  at a particular mole fraction  $\alpha_i = 1$ .

The unit for  $\bar{u}$  and  $u_i^0$  is  $10^{-4} \text{ cm}^2\text{s}^{-1}\text{V}^{-1}$ . The terms "migration of an ion" or "migration mobility" are applied to a motion of an ion  $i$  ( $v_i$ ) or to a motion of an equilibrium system ( $\bar{v}$ ) under the given experimental conditions. The migration mobility is the initial experimental quantity measured during electrophoresis. Its unit is  $\text{cm}\cdot\text{s}^{-1}$ .

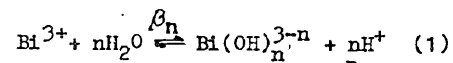
The ion mobility  $u_i^0$  is proportional to equivalent conductivity  $\lambda_i^0 = F \cdot u_i^0$  where the proportion factor  $F$  is Faraday's constant. It allows to compare the obtained values of  $u_i^0$  with  $\lambda_i^0$  data determined by this or that method and published elsewhere.

To denote anion and cation mobility, we used the signs (-) and (+), respectively.

## Results and Discussions

The results of experimental determination of radiobismuth ion mobility in acid and alkaline solutions are shown in Figs. 2 and 3, respectively.

The pH dependence of the overall ion mobility indicates a shift to the right of the equilibrium reactions described by equation (1) when concentration of hydrogen ions in the solution reduces:



where  $n=1,2,3,4$ , and  $\beta_n = \prod_{n=1}^n K_n$  are the stoichiometric equilibrium constants.

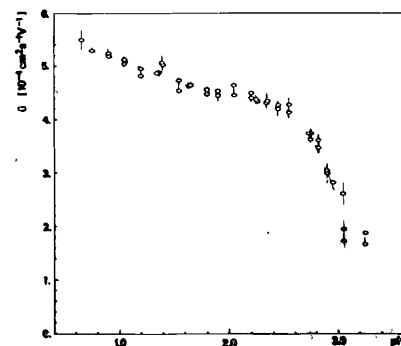


Fig. 2. Overall ion mobility  $\bar{u}_{\text{Bi(III)}}$  as a function of pH in acid solutions of  $\text{Na(H)ClO}_4$ ;  $\mu=0.25 \text{ M}$ ,  $T = 298.1 \text{ K}$ .

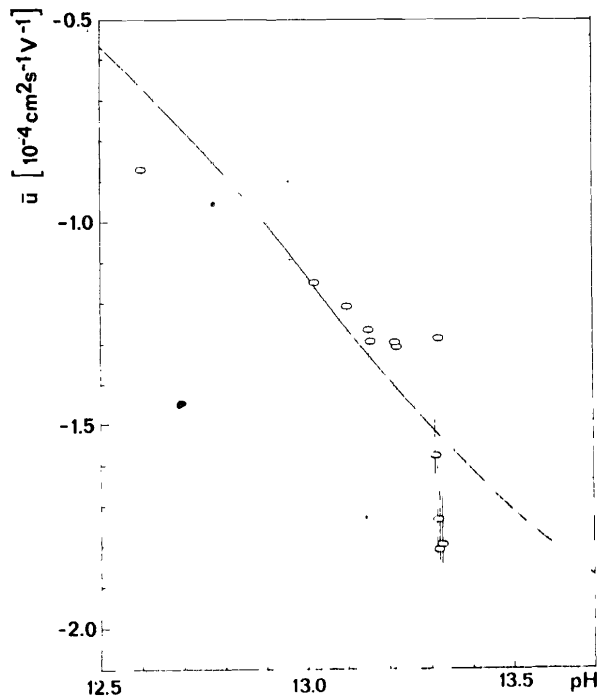


Fig. 3. Overall ion mobility  $\bar{u}_{\text{Bi(III)}}$  as a function of pH in solutions  $\text{NaClO}_4/\text{NaOH}$ ;  $\mu = 0.25 \text{ M}$ ,  $T = 298.1 \text{ K}$ .

The experimental results in Fig. 3 evidently confirm existence of an anionic hydroxide complex of Bi(III) in alkaline solutions. Thus, the same method yields information on the region of existence and ion mobility of four Bi(III) hydrolysis compounds.

When interpreting our experimental data, we make the following assumptions:

Firstly, the value of  $\bar{u}$  is not affected by formation of Bi(III) complexes with  $\text{ClO}_4^-$  and  $\text{CO}_3^{2-}/\text{HCO}_3^-$  anions due to relatively small concentration of perchlorate ions (0.25 M) and a low level of carbonate ion impurity in the fresh prepared solutions.

Secondly, a change in the value of  $\bar{u}$  only indicates formation of monomeric hydrolysis products of bismuth since in our case the concentration of the element in the active zone was  $\leq 10^{-12} \text{ M}$ , and it is known from other publications /8/, that polymeric products of Bi(III) hydrolysis are not observed at concentrations  $\leq 10^{-5} \text{ M}$ .

Finally, presence of  $\text{Na}^+$  and  $\text{ClO}_4^-$  ions in the solutions, affects neither ion mobility, nor chemical properties of Bi(III) ions.

The dependence  $\bar{u} = f([\text{H}^+])$  for the equilibrium system  $\text{Bi}^{3+} \rightleftharpoons \text{Bi}(\text{OH})^{2+} \rightleftharpoons \text{Bi}(\text{OH})_2^+ \rightleftharpoons \text{Bi}(\text{OH})_3$  can be described in general by a sum of particular mole fractions ( $\alpha_i$ ) multiplied by their individual ion mobilities (eq. (2)):

$$\bar{u} = \sum_{n=0}^n \alpha_{\text{Bi}(\text{OH})_n^{3-n}} \cdot u_{\text{Bi}(\text{OH})_n^{3-n}}^0, \quad (2)$$

where  $n = 0, 1, 2, 3$ .

Taking into account eq.(1) and the fact that  $u_{\text{Bi}(\text{OH})_3}^0 = 0$ , eq. (2) can be transformed into eq. (3):

$$\bar{u} = \frac{u_{\text{Bi}^{3+}}^0 \cdot [\text{H}^+]^3 + u_{\text{Bi}(\text{OH})_2^+}^0 \cdot [\text{H}^+]^2 K_1 + u_{\text{Bi}(\text{OH})_2^+}^0 \cdot [\text{H}^+] K_1 K_2}{[\text{H}^+]^3 + [\text{H}^+]^2 K_1 + [\text{H}^+] K_1 K_2 + K_1 K_2 K_3}. \quad (3)$$

Eq. (3) can be used for calculations of its six unknown values - individual hydrolysis constants ( $K_n$ ) and individual ion mobilities ( $u_{\text{Bi}(\text{OH})_n^{3-n}}^0$ ) of the Bi(III) cation - by the least squares method using minimization program MINUIT /16/ at a CDC-6500 computer. The results of these calculations are given in Table 2A.

The calculated curve (Fig. 2) is in good correlation with the experimental data. The values of  $K_n$  obtained in mathematical processing of our experimental results are close to or coincide (in the order of magnitude) with the published data on Bi(III) hydrolysis constants (Table 1). Our calculations allowed us to obtain unique information on the ion mobilities of Bi(III) cation in aqueous solutions. The higher individual ion mobility of  $\text{Bi}(\text{OH})_2^+$  as compared with  $\text{Bi}^{3+}$  and  $\text{BiOH}^{2+}$  is of particular interest. This is an unexpected result as far as the universally accepted ideas /17-25/ of correlation between ion mobility values, their properties and properties of media where they migrate are concerned. According to Stokes' law, individual ion mobilities of the  $\text{Bi}^{3+}$  cation and its hydrolysis products ( $u_i^0$ ) should depend on their charges ( $z_i$ ) and radii ( $r_i$ ) in the following way:

$$u_i^0 = \text{const} \cdot z_i / r_i. \quad (4)$$

If we admit that radii of the bismuth hydroxide ions are equal due to hydration, the ratio of their individual ion mobilities should be as follows:

$$u_{\text{Bi}^{3+}}^0 : u_{\text{Bi}(\text{OH})_2^+}^0 : u_{\text{Bi}(\text{OH})_2^+}^0 = 3:2:1.$$

But mathematical treatment of the experimental function  $\bar{u} = f([\text{H}^+])$  using the fixed mobility ratios leads to a significant difference of  $K_2$  and  $K_3$  values from those published earlier (Table 2B). Thus, the evidently correct values of individual hydrolysis constants of Bi(III) obtained by a free choice of the six constants in Eq. 3 allow an assumption that the quantity  $u_{\text{Bi}(\text{OH})_2^+}^0 = +5.94(8) \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$  is also correct.

Strictly speaking, we cannot exclude the fact that there is an effect owing to which variations of  $\bar{u}$  do not correspond to our

hydrolysis model and, consequently, mathematical treatment of the obtained pH-dependence of  $\bar{u}$  leads to an incorrect value of the mobility of the Bi(III) single-charged hydrolysis cation. In general, this effect may consist in a higher absorption of hydrolysis products on glass, which is well-known for multicharged ions of metals /26-34/.

**Table 2.** Values of hydrolysis constants and individual ion mobilities of Bi(III) in Na(H)ClO<sub>4</sub> electrolytes. 0.75 ≤ pH ≤ 3.25; μ = 0.25 M; T = 298.1 K. Results of mathematical treatment of the experimental function  $\bar{u} = f([H^+])$  using the minimization program MINUIT /16/.

n	pK <sub>n</sub> (K <sub>n</sub> in mol·l <sup>-1</sup> )	General correlation coefficient	u <sup>0</sup> <sub>Bi(OH)<sub>n</sub><sup>3-n</sup></sub> (10 <sup>-4</sup> cm <sup>2</sup> s <sup>-1</sup> v <sup>-1</sup> )	General correlation coefficient
0			+ 5.67(10)	0.848
1	1.40(5)	0.807	+ 3.61(9)	0.803
2	2.17(10)	0.746	+ 5.94(8)	0.325
3	2.84(2)	0.279	0	
$\chi^2 = 0.2335E + 02$				
0			+ 5.67	
1	1.51(3)	0.009	+ 3.78	
2	6.38(4)	0.147	+ 1.89	
3	-0.008(40)	0.147	0	
$\chi^2 = 0.1118E + 03$				

A. Free choice of parameters in Eq. (3).

B. Fixed values of individual ion mobilities.

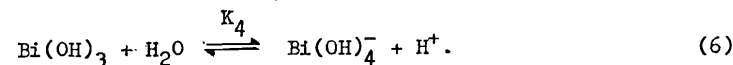
On the other hand, however, we do not have sufficient information on actual relations between physical and chemical properties of ions in aqueous solutions and values of their ion mobility. It is obvious that at the successive deprotonation of the Bi(H<sub>2</sub>O)<sub>x</sub><sup>3+</sup> not only the charge and structure, but also the specific microviscosity and surface charge density of an ion are changed. We think it is quite probable that the second stage of hydrolysis produces a bismuthyl

cation:



This cation with low density of surface charge is weakly hydrated; that is why it may have a relatively high individual ion mobility.

We have mentioned above that we investigated anion products of hydrolysis in strong alkaline solutions (pH > 12.6). We assume that under those conditions equilibrium is most likely only between two hydrolysed forms of Bi(III):



Then Eq.(7) is valid for calculation of overall ion mobility:

$$\bar{u} = \frac{u_{\text{Bi(OH)}_4^-}^0 \cdot K_4}{[H^+] + K_4} \quad (7)$$

Mathematical treatment of the experimental data on dependence of  $\bar{u}$  upon  $[H^+]$  with the use of the program MINUIT /16/ yielded the following values of the constants in Eq.(7):  $u_{\text{Bi(OH)}_4^-}^0 = -2.25(30) \cdot 10^{-4} \text{ cm}^2\text{s}^{-1}\text{v}^{-1}$  and  $K_4 = 8.5(2) \cdot 10^{-14} \text{ mol}\cdot\text{l}^{-1}$  ( $\text{p}K_4 = 13.07(16)$ ).

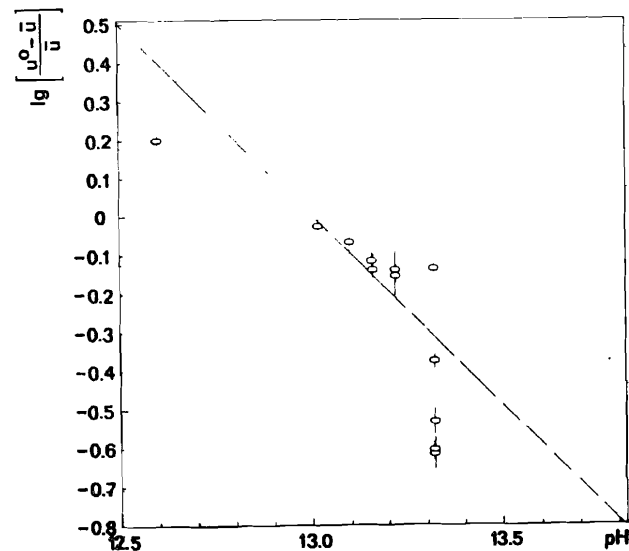


Fig. 4. See explanation in the text.

The value of the hydrolysis constant practically coincides with the one obtained earlier by the solubility method <sup>7/8/</sup>. The calculated curve is in satisfactory correlation with the experimental data (Fig. 3). Increase in the overall ion mobility with increase in pH indicates a rightward shift of reaction (5) equilibrium. However, increase in alkali concentration did not result in higher  $\bar{u}$  in our experiments: in 0.25 M NaOH the overall ion mobility was  $-1.69(13)$ , in 0.4 and 0.5 M alkali it was  $-1.70(9)$  and  $-1.71(15) \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ , respectively.

A higher anionic overall ion mobility of bismuth in the equilibrium system was probably compensated by the stopping effect related to increase in the overall ionic strength of the solution. If Eq.(7) is transformed into a linear one:

$$\lg \left[ \frac{u_{\text{Bi}(\text{OH})_4^-}^0}{\bar{u}} - \bar{u} \right] = \text{p}K_4 - \text{pH} \quad (8)$$

the calculated points will be near a straight line that has a slope of -1 and runs through 0 at minimal  $\chi^2$  at  $\text{p}K = 13.03$  (Fig. 4).

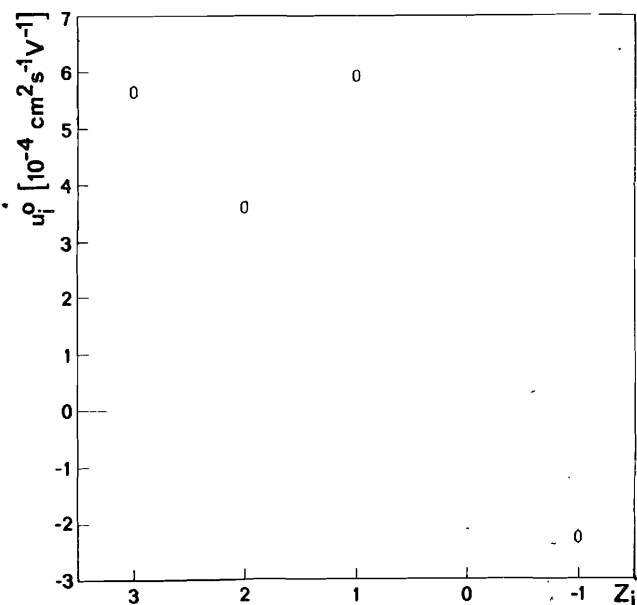


Fig. 5. Individual ion mobility of monometric hydrolysis products of Bi(III) as a function of the ion charge.

We think that this result proves the assumption that only one anionic Bi(III) hydroxyle complex is produced in the alkaline solutions investigated.

Analysis of ratios of  $u_{\text{Bi}(\text{OH})_n}^0$  values of ions with  $n=0,1,3,4$  (Fig. 5) allows a conclusion that a simple linear relationship is valid for them:

$$u_{\text{Bi}(\text{OH})_n}^0 = 1.98(18) \cdot (3-n) \quad (9)$$

### Conclusion

Measurements of carrier-free radiobismuth electromigration in free electrolytes followed by mathematical treatment of experimental data allowed for the first time to obtain individual ion mobility values for  $\text{Bi}(\text{OH})_n^{3-n}$  bismuth ions with the charges  $3^+$ ,  $2^+$ ,  $1^+$  and  $1^-$  and values of individual hydrolysis constants using one and the same method. The highest individual ion mobility was observed for the single-charged cation, which allows a conclusion that a monomeric cation  $\text{BiO}^+$  exists under our experimental conditions.

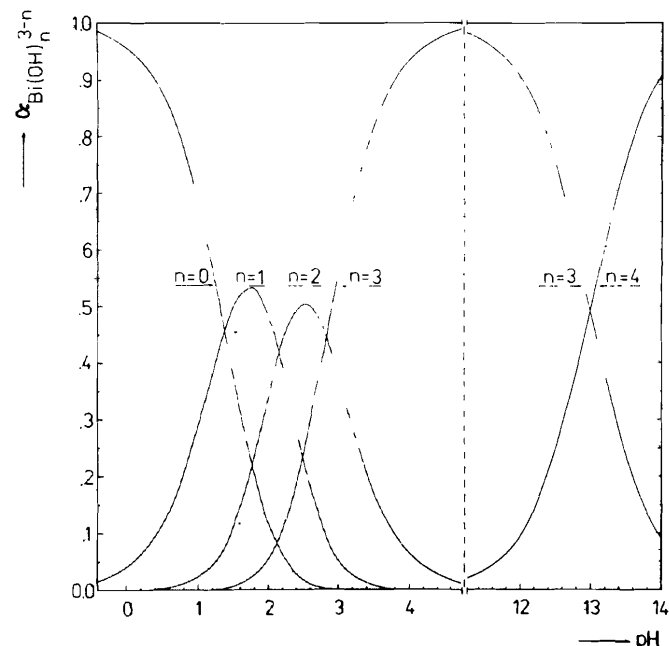


Fig. 6. Relative quantities of the monomeric hydrolysis products  $\text{Bi}(\text{OH})_n^{3-n}$  ( $n = 0-4$ ) in solutions with  $\mu = 0.25 \text{ M}$  and  $T = 298.1 \text{ K}$  as a function of pH.

It has become possible to carry out the experiments with radio-bismuth because in the electromigration tube the temperature was automatically regulated during the experiment and the initial pH of the solution was maintained, which was not the case in previous electromigration investigations /35-48/. Fig. 6 shows equilibrium concentrations of bismuth hydroxyle complexes in solutions with  $\mu = 0.25$  M at  $T = 298.1$  K as a function of pH; basing on the hydrolysis constants obtained. Those concentrations practically coincide with those published earlier /50/ and differ from them by an insignificant ( $\Delta\text{pH} \leq 0.3$ ) shift toward the alkaline region.

Success in investigation of Bi(III) properties shows that our electromigration set-up can be widely employed for studying processes of hydrolysis and complex formation of various elements at their ultramicroconcentrations in solutions.

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#### References

- Olin A., Acta Chem.Scand., 1959, 13, 1791
- Taube R.S., Tyree S.Y., J.Amer.Chem.Soc., 1960, 82, 3244
- Gattow G., Schott D., Z.Anorg.Chem., 1963, 324, 31
- Dragalescu C., Nimara A., Julean I., Rev.Romaine Chim., 1974, 19, 1455
- Goward G.W., Thesis, Princeton 1954, Uni Microfilms 9414
- Olin A. Acta Chem.Scand., 1957, 10, 476
- Van Mylder J., Porraux M., Proc. 9th Meeting Int.Commen. Electrochem.Therma Kinetics, 47 London, 1956, 76
- Bildeman T.A., Analyt.Chim.Acta, 1971, 56, 221
- Dragalescu C., Nimara A., Julean I., Chem.Analit. 1972, 17, 631
- Antonovitch V.M., Nevskaya E.M., Schelichina E.N. et al., Zh.Neorg.Khim, 1975, 20, 2968
- Nimara A., Julean I., Rev.Romaine Chim., 1977, 22, 691
- Milanov M., Doberenz W., Dreyer R., Noak M., Khalkin V.A., Radiokhimiya, 1982, 24, 520
- Milanov M., Doberenz W., Marinov A., Khalkin V.A., J.Radioanal. Nucl.Chem., 1981, 82, 101
- Milanov M., Marinov A., Tran Kim Hung, Doberenz W., Khalkin V.A., Rep.JINR 6-83-209, Dubna, 1983
- Erlitchenko V.P., Vinogradova V.G., Sevast'janov Yu.G., Atomnaya energiya, 1969, 27, 349
- James F., Roos M., CERN Computer 6000 Series Program Library, Long-Write-Up D506, D516 (1971)
- Walden P., Das Leitvermögen der Elektrolyte, in: Handbuch der Allgemeinen Chemie, Bd.II, Herausgeber: Ostwald-Drucker, Akademische Verlagsgesellschaft m.b.H. Leipzig, 1924
- Kortüm G., Elektrolytlösungen, Becker u. Erlter, Leipzig, 1941
- Falkenhagen H., Ergebnisse der modernen Elektrolytforschung, Akademie-Verlag, Berlin 1957
- Fuoss M.R., Accascina F., Electrolytic Conductance, Interscience Publ., New York, 1959.
- Robinson R.A., Stokes R.H., Electrolytic Solutions, Butterworth, London, 1959
- Harned H.S., Owen B.E., The Physical Chemistry of Electrolytic Solutions, Reinhold Publ., London, 1963
- Müchel W., Die Entwicklung der Hypothese vom nichtklassischen Ion, Springer-Verlag, Berlin 1968
- Falkenhagen H., Theorie der Elektrolyte, S.Hirzel-Verlag, Leipzig, 1971
- Schwabe K., Elektrochemie, Akademie-Verlag, Berlin 1975
- Kraus K.A., Nelson F., J.Amer.Chem.Soc., 1950, 72, 3901
- Stryker L.J., Metijevic E., Colloid Interface Sci., 1961, 31, 39
- Matijevic E. et al., J.Phys.Chem., 1961, 65, 1724
- Hahn O., Stumm W., Advan.Chem.Ser., 1968, 79, 91
- Benes P., Rajman I., Coll.Czech.Chem.Comm., 1969, 34, 1375
- Starik I.E. et al., Radiokhimiya, 1961, 3, 428
- Benes P., Coll.Czech.Chem.Comm., 1970, 35, 1349
- Starik I.E. et al., Radiokhimiya, 1959, 1, 37
- Benes P., Majer V., Trace Chemistry in Aqueous Solution, Akademia, Prague, 1980
- Stepanov A.V., Makurova T.P., Radiokhimiya, 1967, 2, 58
- Hein R.E. et al., Analyt.Chem., 1956, 28, 544
- Suchotina G.G., Suchotin A.M., Zh.Fiz.Khim., 1961, 35, 41
- Inselt E., Lengyel S., Acta Chim.Hung., 1963, 35, 407
- Dreyer I., Dreyer R., Khalkin V.A., Radiochem.Radioanal.Letters, 1973, 33, 291; 1978, 35, 257; 1978, 36, 389.
- Dreyer I., Dreyer R., Khalkin V.A., Milanov M., Radiochem. Radioanal.Letters, 1979, 40, 145
- Dreyer R., Dreyer I., Rösch F., Beyer G.-J., Radiochem. Radioanal.Letters, 1982, 54, 165
- Dreyer R., Rösch F., Beyer G.-J., Wissenschaft und Fortschritt, 1982, 32, 251

43. Dreyer R., Dreyer I., Rösch F., Z.Chem., 1982, 22, 54  
 44. Dreyer R., Dreyer I., Pfeiffer M., Rösch F., Radiochem. Radioanal.Letters, 1982, 55, 207  
 45. Dreyer R., Dreyer I., Rösch F., Fischer S., Z.Chem., 1983, 23, 346  
 46. Rösch F., Thesis, Techn.Univ.Dresden, Dresden, 1984  
 47. Rösch F., Dreyer R., Dreyer I., Fischer S., 12th Int. Hot Atom Chem.Symp.Balatonfüred, 23-28 Sept.1984, Hungary, Abstracts p. 64  
 48. Milanov M., Doberenz W., Khalkin V.A., Marinov A., J.Radioanal. Nucl.Chem., Articles, 1984, 83, 291  
 49. Vasiliev D., Salamatin A.V. Rep.JINR, P10-85-189, Dubna, 1985  
 50. Nasarenko V.A., Antonovitch V.P., Nevskaya E.I., Hydrolysis of metal ions in dilute solutions, Atomizdat, Moscow, 1979, p. 122

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Электромиграция ионов радионуклидов без носителей в электролитах. Гидролиз Bi(III) в водных растворах

Исследована электромиграция ионов радиовисмута-205, 206 без носителя в постоянном электрическом поле. Получены данные о зависимости подвижности ионов висмута от pH при ионной силе 0,25 и температуре 298,1(1)K. Исходя из этих данных, в соответствии с равновесными гидролитическими процессами мономерных соединений висмута рассчитаны константы гидролиза и подвижности ионов висмута в перхлоратных растворах. Обнаружена относительно высокая подвижность однозарядного катиона  $\text{Bi}(\text{OH})_2^+$ . Это позволяет сделать предположение о существовании в водных растворах мономерного катиона висмутила.

Работа выполнена в Лаборатории ядерных проблем ОИЯИ.

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Electromigration of Carrier-Free Radionuclide Ions in Electrolytes. Hydrolysis of Bi(III) in Aqueous Solution

The electromigration of carrier-free <sup>205,206</sup>Bi ions in a constant electric field has been investigated. Results about dependence of bismuthium ion mobilities on pH have been obtained at overall ionic strength 0.25 M and temperature 298.1(1)K. Basing on this results hydrolysis constants and individual ion mobilities of bismuthium species have been calculated according to the hydrolysis processes of monomeric bismuthium. A relative high ion mobility of the monovalent bismuthium cation  $\text{Bi}(\text{OH})_2^+$  has been detected. This may be interpreted by the existence of monomeric bismuthyl cation in aqueous solutions.

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

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