

ANALYTICAL DATA

ELECTROMIGRATION OF CARRIER-FREE RADIONUCLIDE IONS

BISMUTH COMPLEXES IN AQUEOUS SOLUTIONS OF OXALIC, FUMARIC AND SUCCINIC ACIDS

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Summary—The overall ion mobilities \bar{u} of carrier-free radiobismuth have been measured in aqueous solutions of some dicarboxylic acids (H₂L)—oxalic, fumaric and succinic—by means of a new version of the electromigration method in electrolytes consisting of HClO₄/H₂L, 0.20*m* H⁺, $\mu = 0.20m$; Na(H)ClO₄/H₂L, 0.05*m* H⁺, $\mu = 0.20m$; Na(H)ClO₄/H₂L, 0.05*m* H⁺, $\mu = 0.25m$; at 298.15 K. Mathematical processing of the experimental functions $\bar{u} = f([L^{2-}])$ allowed calculation of the mean individual stability constants K_n and ion mobilities u° of the complex ions [BiL_{*n*}]^{3-2*n*}, *n* = 1, 2: [Bi(C₂O₄)]⁺, log $K_1 = 7.65$ (8), $u^\circ = +2.26$ (5) × 10⁻⁴ cm². sec⁻¹. V⁻¹; [Bi(C₂O₄)₂]⁻, log $K_2 = 4.81$ (2), $u^\circ = -1.63$ (64) × 10⁻⁴ cm². sec⁻¹. V⁻¹; [Bi(C₄O₄H₂)]⁺, log $K_1 = 6.90$ (20); [Bi(C₄O₄H₄)]⁺, log $K_1 = 8.76$ (48).

The electromigration method, used to measure the ion mobilities of elements in a constant electric field, is very suitable for determination of stability constants for metal-ion complexes in solution, especially for carrier-free radionuclide concentrations of the elements.¹⁻³ In earlier work⁴ we investigated hydrolysis of Bi(III) in acidic and alkaline sodium perchlorate solutions, using a special horizontal electrophoresis technique. This modified version of the electromigration method, which avoids use of finely divided inert materials such as quartz sand for hydrodynamic stabilization of the electrolyte, has been developed in our laboratory.⁵⁻⁷ A new design of the electromigration cell ensures stability of the chemical composition of electrolytes and also temperature stability during prolonged measurements. It also excludes the occurrence of liquid fluxes in the tube along which the ions are moving.

The results of the first radiobismuth experiments showed that it is reasonable to use this technique for studying not only hydrolysis, but also formation of metal-ion complexes with various ligands.

The aim of the work described in this paper was to determine the stability constants of the mononuclear bismuth complexes with dicarboxylic (oxalic, fumaric, succinic) acids. Bismuth complexes of this type are poorly studied, compared with those of other metals. This is evidently due to difficulties in processing and interpreting the experimental results, since the investigations are performed in slightly acidic or neutral solutions where two processes occur at the same time: complex formation and hydrolysis of the bismuth cation Bi³⁺. The available literature data, obtained with only one analytical technique for one ligand, seemed to us to be worth checking.

Table 1 lists the available data on the stability constants of bismuth complexes with dicarboxylic acids.

EXPERIMENTAL

The investigations were performed with carrier-free ^{205,206}Bi radionuclides.

Table 1. Stability constants of bismuth complexes with dicarboxylic acids H₂L

Acid (H ₂ L)	<i>T</i> , K	μ ; electrolyte; pH	Equilibrium reaction	log K_1	log K_2	log K_3	Ref.
Oxalic	293.1	0.01; HClO ₄ ; 2.0	Bi ³⁺ + L ²⁻ ⇌ BiL ⁺	6.1			8
Oxalic	298.1	1.0; KNO ₃ ; 2.33	Bi ₂ L ₃ + 2L ²⁻ ⇌ BiL ₂ ⁻ + BiL ₃ ⁻		(log $\beta_2 = 8.38$) (log $\beta_3 = 8.15$)		8
Malic	298.1	3.0; Na ₂ SO ₄ ; 4.5	Bi ³⁺ + 5HL ⁻ ⇌ Bi(HL) ₅ ³⁻			(log $\beta_5 = 16.53$)	9
Tartaric	298.1	3.0; Na ₂ SO ₄ ; 3.0	Bi ³⁺ + HL ⁻ ⇌ Bi(HL) ₂ ²⁺	7.56			9
Aspartic	298.1	0.1; NaClO ₄ ; 2.6-9.0	Bi ³⁺ + <i>n</i> L ²⁻ ⇌ BiL _{<i>n</i>} ^{3-2<i>n</i>}	10.47	8.65	3.67	10
Glutamic	298.1	0.1; NaClO ₄ ; 2.6-9.0	Bi ³⁺ + <i>n</i> L ²⁻ ⇌ BiL _{<i>n</i>} ^{3-2<i>n</i>}	10.47	8.28	3.50	10

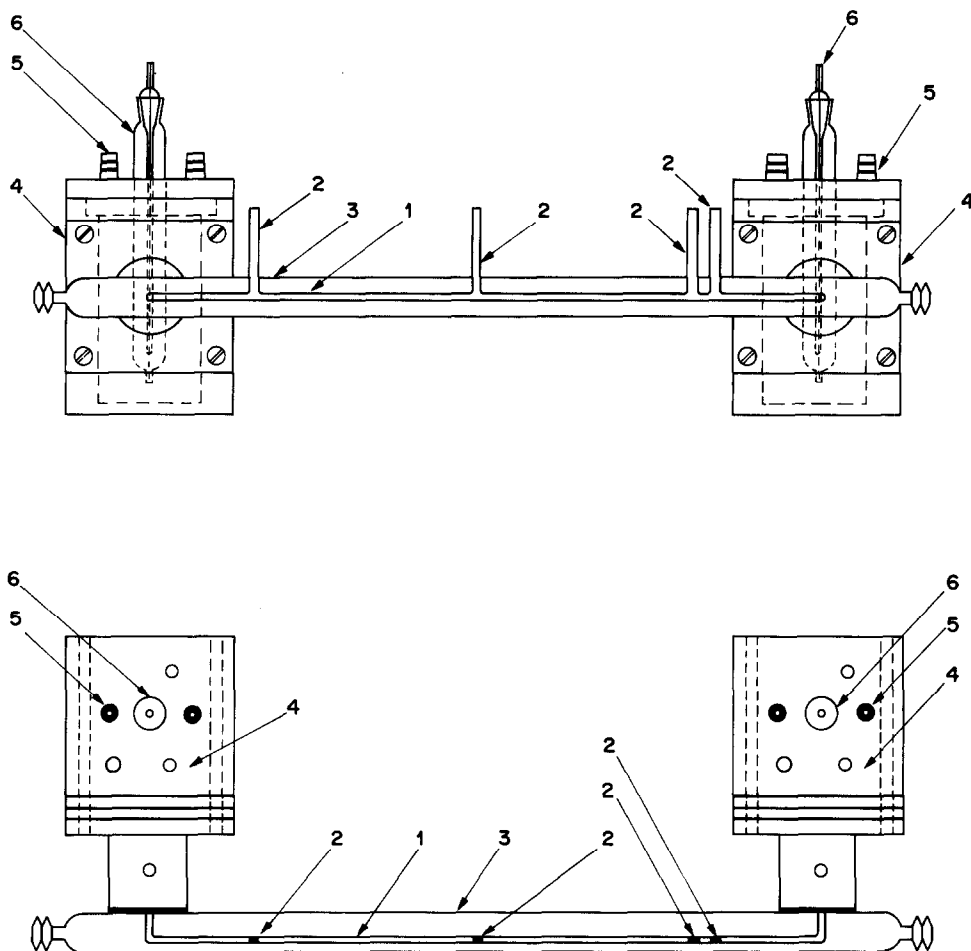


Fig. 1. Lay-out of the electromigration cell: 1—electromigration tube of glass; 2—outlets to insert a thermosensor and voltage-measuring electrodes and inject radionuclide solutions; 3—thermostatic casing; 4—electrode chambers; 5—tubes to supply water for cooling electrode chambers; 6—platinum electrodes.

Radiobismuth was obtained by exposure of natural lead to 65-MeV protons in the isochronous cyclotron U-240, INR Academy of Sciences of the Ukrainian SSR (Kiev). Radiobismuth was separated from lead, then purified and concentrated by known techniques.¹² The specific activity of the final ^{205,206}Bi solution in 0.1*m* nitric acid was about 10 GBq/ml.

The electromigration cell is schematically shown in Fig. 1. A detailed description of the experimental procedure is given in our previous papers.⁴⁻⁷

The overall ion mobilities of bismuth were measured at 298.15(10) K in the following electrolyte systems, containing oxalic, fumaric and succinic acids (H₂L): (I) HClO₄/H₂L, 0.200*m* H⁺, $\mu = 0.200$ (2); (II) Na(H)ClO₄/H₂L, 0.050*m* H⁺, $\mu = 0.200$ (5); (III) Na(H)ClO₄/H₂L, 0.050*m* H⁺, $\mu = 0.250$ (5). The L²⁻ concentrations varied from 0 to 2×10^{-4} *m*, 7.5×10^{-7} *m* and 4×10^{-8} *m* for C₂O₄²⁻, C₄O₄H₂²⁻ and C₄O₄H₄²⁻, respectively. Electrolyte solutions were prepared in doubly distilled water with chemically pure and analytical grade reagents.

The electromigration tube and the electrode chambers were filled with electrolyte of given composition, and 1–2 μ l of the ^{205,206}Bi stock solution was injected.

The electromigration of radiobismuth, building up equilibrium systems corresponding to the electrolyte com-

position, was monitored by detecting the gamma-radiation of ^{205,206}Bi by means of a gliding scintillation detector. The electric field-strength gradient was kept constant in all experiments: $\Delta E = 10.00$ (5) V/cm. The experimental set-up allowed continuous measurement of the radiobismuth velocity (cm/sec) along the tube. These values were then used for calculation of the overall ion mobilities (u , 10^{-4} cm²·sec⁻¹·V⁻¹) in the given systems.

RESULTS AND DISCUSSION

Formation of Bi(III) complexes with oxalate

Figure 2 shows the results obtained for the experimental dependence of the overall bismuth ion mobility $\bar{u}_{\text{Bi(III)}}$ on C₂O₄²⁻ concentration in 0.200 and 0.050*m* solutions of H⁺ at constant overall ionic strength $\mu = 0.200$ (electrolyte systems I and II). Concentrations of oxalate were calculated on the basis of the oxalic acid dissociation constants $pK_{01} = 1.31$, $pK_{02} = 3.81$.¹¹

To simplify the calculation of the stability constants we assumed that the complex formation occurs

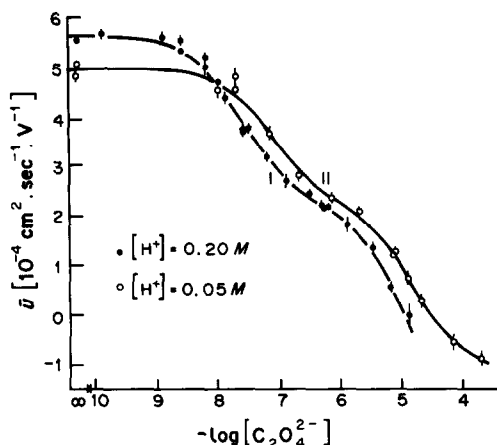
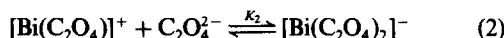
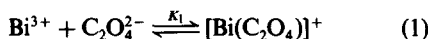


Fig. 2. Overall ion mobility of carrier-free radiobismuth in aqueous solutions of oxalic acid/H(Na)ClO₄; $\mu = 0.200$, $T = 298.15$ (10) K. (I, $[H^+] = 0.200m$; II, $[H^+] = 0.050m$; solid lines are the calculated curves).

only according to reactions (1) and (2):



We also assumed that other ions in the systems under investigation, as well as protonated oxalate species, do not markedly affect the radiobismuth electromigration. These assumptions allowed formulation of equation (3), which takes into account the influence of both of the complex formation reactions and of the Bi(III) hydrolysis on the overall ion mobility \bar{u} of Bi(III):

$$\bar{u} = \frac{u_1^{\circ}[H^+]^3 + u_2^{\circ}K_1'[H^+]^2 + u_3^{\circ}K_1'K_2'[H^+] + u_4^{\circ}K_1[L^{2-}][H^+]^3 + u_5^{\circ}K_1K_2[L^{2-}]^2[H^+]^3}{[H^+]^3 + K_1'[H^+]^2 + K_1'K_2'[H^+] + K_1'K_2'K_3' + K_1[L^{2-}][H^+]^3 + K_1K_2[L^{2-}]^2[H^+]^3} \quad (3)$$

Table 2. Values of complex formation parameters in equation (4) obtained after mathematical processing of experimental dependences $\bar{u} = f([C_2O_4^{2-}])$ in the electrolyte systems I and II [here and elsewhere in the paper, the numbers in brackets are the standard deviations of the results and refer to the last figure(s) quoted]

Parameter	Electrolyte system		Mean values
	I (0.200m H ⁺)	II (0.050m H ⁺)	
log K_1	7.67 (2)	7.40 (7)	7.65 (8)
log K_2	4.92 (2)	4.81 (7)	4.81 (2)
log β_2	12.59 (34)	12.21 (13)	12.46 (5)
$u_{[Bi(C_2O_4)]^+}^{\circ}$ (10^{-4} cm ² .sec ⁻¹ .V ⁻¹)	+2.26 (4)	+2.24 (11)	+2.26 (5)
$u_{[Bi(C_2O_4)_2]^-}^{\circ}$ (10^{-4} cm ² .sec ⁻¹ .V ⁻¹)	-2.55 (21)	-1.18 (15)	-1.63 (64)
C_1 (10^{-4} cm ² .sec ⁻¹ .V ⁻¹)	6.66 (4)	10.33 (8)	
C_1^* (10^{-4} cm ² .sec ⁻¹ .V ⁻¹)	6.34	7.90	
C_2	1.184 (8)	2.064 (18)	
C_2^*	1.205	1.902	

At $[L^{2-}] = 0$, $\bar{u}_{Bi(III)} = +5.64$ (4) $\times 10^{-4}$ cm².sec⁻¹.V⁻¹ (I), and $+5.00$ (5) $\times 10^{-4}$ cm².sec⁻¹.V⁻¹ (II), respectively. C_1^* and C_2^* are calculated from the hydrolysis data given earlier.⁴

where u_i° and K_i' ($i = 1, 2, 3$) are the individual ion mobilities and individual stoichiometric hydrolysis constants for $[Bi(OH)_i]^{3-i+}$ species and u_4° , u_5° , K_1 and K_2 are the individual ion mobilities and stoichiometric complex formation constants of $[BiL_n]^{3-2n}$ ions with ligands L^{2-} and $n = 1, 2$. Equation (3) can be reduced to a more compact form (4).

$$\bar{u} = \frac{C_1 + u_4^{\circ}K_1[L^{2-}] + u_5^{\circ}K_1K_2[L^{2-}]^2}{C_2 + K_1[L^{2-}] + K_1K_2[L^{2-}]^2} \quad (4)$$

where C_1 and C_2 represent the bismuth hydrolysis data:

$$C_1 = u_1^{\circ} + u_2^{\circ}K_1'[H^+]^{-1} + u_3^{\circ}K_1'K_2'[H^+]^{-2}$$

$$C_2 = 1 + K_1'[H^+]^{-1} + K_1'K_2'[H^+]^{-2}$$

$$+ K_1'K_2'K_3'[H^+]^{-3}$$

Equation (4) allows calculation of the individual ion mobilities and stability constants of bismuth complexes without knowledge of the Bi(III) hydrolysis data in the electrolyte systems I and II, since these data can be treated as unknowns to be evaluated in the data-processing. This equation was used for mathematical processing of the experimental results by the least-squares method with the minimizing program MINUIT,¹³ its six unknown parameters being calculated on a CDC-6500 computer. The calculation results are listed in Table 2.

The solid lines in Fig. 2 show the curves calculated by means of the parameters obtained. They fit well with the experimental points.

It follows from the data of Table 2 that the values of K_1 and K_2 and the individual ion mobility of the $[Bi(C_2O_4)]^+$ complex cation were similar for electrolytes I and II, but the individual ion mobility of the

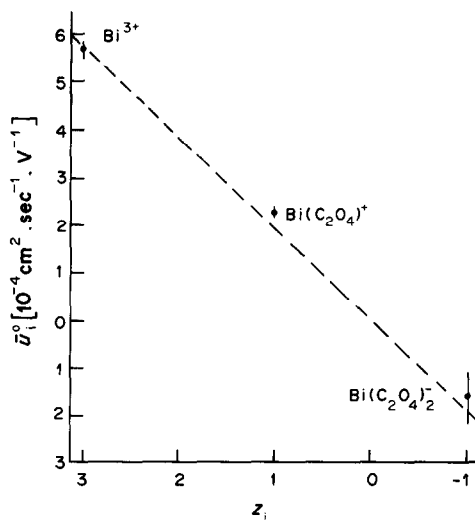


Fig. 3. Individual ion mobilities of Bi^{3+} , $[\text{Bi}(\text{C}_2\text{O}_4)]^+$ and $[\text{Bi}(\text{C}_2\text{O}_4)_2]^-$ as a function of ion charge ($u_{\text{Bi}^{3+}}$ from previous work⁴).

$[\text{Bi}(\text{C}_2\text{O}_4)_2]^-$ anion is only half as large in system II as in system I. The value from system II is probably the more reliable, since the maximum concentration of $\text{C}_2\text{O}_4^{2-}$ is one order of magnitude higher than in system I: $1.99 \times 10^{-4} m$ and $1.24 \times 10^{-5} m$, respectively.

Table 2 also lists values of parameters C_1^* and C_2^* calculated on the basis of the data previously obtained for the hydrolysis constants and individual ion mobilities for Bi(III) hydrolysis in perchlorate solutions with $\mu = 0.250 m$.⁴ It is seen that the two sets of results for electromigration of radiobismuth in solutions of different chemical composition are in good agreement. This allows the conclusion that the calculated individual ion mobilities and stability constants

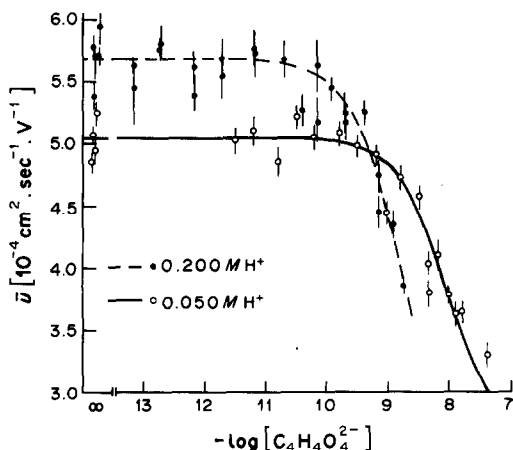


Fig. 4. Overall ion mobility of carrier-free radiobismuth in aqueous solutions of succinic acid/ $\text{H}(\text{Na})\text{ClO}_4$; $\mu = 0.200$, $T = 298.15$ (10) K. (I, $[\text{H}^+] = 0.200 m$; II, $[\text{H}^+] = 0.050 m$; solid lines are the calculated curves).

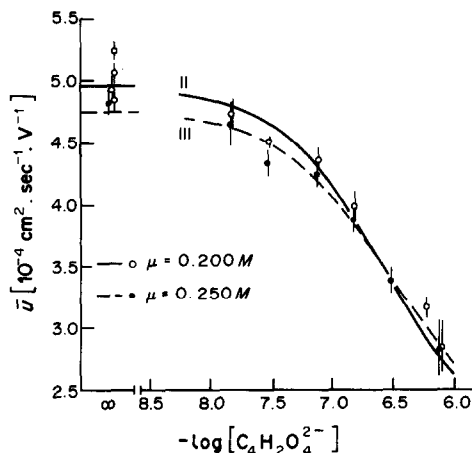


Fig. 5. Overall ion mobility of carrier-free radiobismuth in aqueous solutions of fumaric acid/ $\text{H}(\text{Na})\text{ClO}_4$; $[\text{H}^+] = 0.050 m$, $T = 298.15$ (10) K. (II, $\mu = 0.200 m$; III, $\mu = 0.250 m$; solid lines are the calculated curves).

for the complex $[\text{Bi}(\text{C}_2\text{O}_4)_n]^{3-2n}$, $n = 1, 2$, are probably close to the real values, despite the simplification of the model chosen for processing the experimental data.

On the other hand, the results of the present paper can be treated as confirmation of the fact that the data on bismuth hydrolysis obtained earlier by the electromigration method⁴ are correct.

The individual ion mobilities of Bi^{3+} , $[\text{Bi}(\text{C}_2\text{O}_4)]^+$ and $[\text{Bi}(\text{C}_2\text{O}_4)_2]^-$ calculated in the present paper—and for $\text{Bi}(\text{OH})_n^{3-n}$ ions with $n = 0, 1, 3, 4$, calculated in the previous work⁴—show a distinct linear dependence on the charges of the ions (Fig. 3), which is close to the Stokes law. The correlation can be written as

$$u_{[\text{Bi}(\text{C}_2\text{O}_4)_n]^{3-2n}}^\circ = \text{const.} \times z_{[\text{Bi}(\text{C}_2\text{O}_4)_n]^{3-2n}}, \quad (5)$$

where $n = 0, 1, 2$. This allows the assumption that the ions under consideration have similar radii and electrolyte micro-viscosity in aqueous solutions. Similar experimental dependences have been discussed by other authors.^{2,14}

Formation of Bi(III) complexes with fumarate and succinate

The experimentally measured overall ion mobilities of Bi(III) in electrolytes I and II containing different concentrations of $\text{C}_4\text{O}_4\text{H}_4^{2-}$ (succinate) and electrolyte systems II and III containing $\text{C}_4\text{O}_4\text{H}_2^{2-}$ (fumarate) are shown in Figs. 4 and 5. In calculating the stability constants for the succinate and fumarate complexes, we assumed the complex formation mechanism was similar to that adapted for oxalate as ligand. Mathematical processing was again done by means of the program MINUIT, according to equation (4).

As both fumaric and succinic acids are weak (the $\text{p}\beta_2$ values are 7.41 and 9.08 respectively^{15,16}), it is

Table 3. Values of $\log K_1$ and $\bar{u}_{\text{Bi(III)}}$ (at $[L^{2-}] = 0$), calculated by the mathematical processing of experimental dependences $\bar{u} = f([L^{2-}])$, where L^{2-} represents succinate ($\text{C}_4\text{O}_4\text{H}_4^{2-}$) and fumarate ($\text{C}_4\text{O}_4\text{H}_2^{2-}$) in the electrolyte systems I, II, III

Acid	Parameter	Electrolyte system			Mean value
		I	II	III	
Succinic	$\log K_1$	9.07 (7)	8.27 (9)	—	8.67 (48)
	$\bar{u}_{\text{Bi(III)}} (10^{-4} \text{ cm}^2 \cdot \text{sec}^{-1} \cdot \text{V}^{-1})$	+5.68 (10)	+5.04 (10)	—	—
Fumaric	$\log K_1$	—	6.94 (10)	6.82 (20)	6.90 (20)
	$\bar{u}_{\text{Bi(III)}} (10^{-4} \text{ cm}^2 \cdot \text{sec}^{-1} \cdot \text{V}^{-1})$	—	+4.96 (10)	+4.74 (10)	—

evident that changes in the bismuth overall ion mobility in the electrolytes used were mainly determined by formation of the complex cations $[\text{BiL}]^+$.

Therefore, in performing the calculations, we cannot keep the quantities $u_{[\text{BiL}_n]^{3-2n}}$, $n = 1, 2$, as unknowns in equation (4) and, consequently, have to give them fixed values: $u_{[\text{BiL}]^+} = +2.25(25) \times 10^{-4} \text{ cm}^2 \cdot \text{sec}^{-1} \cdot \text{V}^{-1}$ and $u_{[\text{BiL}_2]^-} = -2.0(1.0) \times 10^{-4} \text{ cm}^2 \cdot \text{sec}^{-1} \cdot \text{V}^{-1}$. These values were chosen on the assumption that complex ions of bismuth with dicarboxylic acid anions have similar individual ion mobility values in aqueous electrolytes with the same (or almost the same) overall ionic strength and the same temperature.

The results are given in Table 3. First it should be noted that similar values of $\log K_1$ were obtained for electrolyte systems of different composition, *i.e.*, of different pH or overall ionic strength, for both the succinate and fumarate complexes. The overall ion mobilities of Bi(III) obtained at $[L^{2-}] = 0$ were practically the same as those for the oxalic acid solutions, or calculated on the basis of our earlier work.⁴

The solid lines in Figs. 4 and 5 show $\bar{u} = f([L^{2-}])$ calculated by equation (4) with parameters obtained in the mathematical processing of the experimental data. As is seen, the curves satisfactorily coincide with the experimental points.

The complex formation of bismuth with fumarate was investigated in two solutions of constant acidity (0.05M H^+) but different values of overall ionic strength (electrolytes II and III). As could be expected, the bismuth overall ion mobilities tended to decrease in electrolyte III ($\mu = 0.250m$).

CONCLUSION

Measurement of the electromigration values of carrier-free radiobismuth in aqueous solutions of dicarboxylic (oxalic, fumaric, succinic) acids at 298.15(10) K has yielded the experimental dependence of the overall ion mobility of bismuth on ligand concentration, $\bar{u} = f([L^{2-}])$. The mathematical (computer) processing of these functions by the least-squares method was based on simplified models of the equilibrium processes of bismuth complex formation and hydrolysis of Bi(III) in the systems under investigation. Mean values of the first and second individual stability constants and the individ-

ual ion mobilities of bismuth oxalate complexes were calculated: $\log K_1 = 7.65(8)$ and $\log K_1 = 4.81(2)$; $u_{[\text{Bi}(\text{C}_2\text{O}_4)]^+} = +2.26(5) \times 10^{-4} \text{ cm}^2 \cdot \text{sec}^{-1} \cdot \text{V}^{-1}$ and $u_{[\text{Bi}(\text{C}_2\text{O}_4)_2]^-} = -1.63(64) \times 10^{-4} \text{ cm}^2 \cdot \text{sec}^{-1} \cdot \text{V}^{-1}$; ($\mu = 0.200$).

The first stability constants of the succinate and fumarate complexes of bismuth are $\log K_1 = 8.67(48)$; ($\mu = 0.200$) and $\log K_1 = 6.90(20)$; ($\mu = 0.200$ and 0.250), respectively.

None of these values was determined earlier, except K_1 for oxalate complexes. Our value for it is almost two orders of magnitude larger than the one in Table 1. Such a significant difference is probably due to improper allowance for bismuth hydrolysis in the earlier work.⁸

The individual ion mobilities u° of Bi^{3+} and its oxalate complexes show a linear dependence on the ionic charge. The dependence can be described by

$$u_{[\text{Bi}(\text{C}_2\text{O}_4)_n]^{3-2n}}^\circ = 1.9(3 - 2n)$$

where $n = 0, 1, 2$, and suggests that the radii and micro-viscosities of the bismuth species are close in value for these ions in the electrolyte systems used.

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REFERENCES

- V. P. Shvedov, *Elektromigratsionnyi metod v fiziko-khimicheskikh issledovaniyach*, Atomizdat, Moscow, 1971.
- A. V. Stepanov and E. K. Kortshemnaja, *Elektromigratsionnyi metod v neorganicheskom analysye*, Khimiya, Moscow, 1979.
- T. P. Makarova and A. V. Stepanov, *Radiokhimiya*, 1977, **19**, 125.
- M. Milanov, F. Rösch, V. A. Khalkin, J. Henniger and Tran Kim Hung, *JINR*, E12-86-144, Dubna, 1986.
- M. Milanov, W. Doberenz, R. Dreyer, M. Noak and V. A. Khalkin, *Radiokhimiya*, 1982, **24**, 520.
- M. Milanov, W. Doberenz, A. Marinov and V. A. Khalkin, *J. Radioanal. Nucl. Chem.*, 1984, **82**, 101.
- M. Milanov, A. Marinov, Tran Kim Hung, W. Doberenz and V. A. Khalkin, *JINR*, 6-83-209, Dubna, 1983.
- H. Ladzinska-Kulinska, *Chemia*, 1975, **31**, 35.
- E. G. Tshirkesova and I. I. Vataman, *Zh. Neorgan. Khim.*, 1970, **15**, 424.

10. M. K. Singh and M. N. Srivastava, *J. Inorg. Nucl. Chem.*, 1972, **34**, 2067.
11. G. M. Armitage and H. S. Sunsmore, *ibid.*, 1973, **35**, 817.
12. V. P. Erlitchenko, V. G. Vinogradova and Yu. G. Sevast'yanov, *Atom. Energiya*, 1969, **27**, 349.
13. F. James and M. Roos, *MINUIT Program*, CERN Computer Centre, Program Library, Long-Write-Up, D-506, D-596 (1971).
14. R. Lundqvist, *Acta Chem. Scand.*, 1981, **A35**, 31.
15. P. G. Manning and S. Ramamoorthy, *J. Inorg. Nucl. Chem.*, 1973, **35**, 1571.
16. Yu. Yu. Lurye, *Spravochnik po analiticheskoy khimii*, Khimiya, Moscow, 1979.