SELF-DIFFUSION OF ^{125}Sb(III) IN AQUEOUS SOLUTIONS

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Formation of hydroxo complexes or Sb(III) hydroxide has been inferred from pH dependence of self-diffusion of ^{125}Sb(III). Temperature dependence within 288 to 298 K gave the activation energy of the self-diffusion of ^{125}Sb(III) 97·4 kJ/mol. Decrease of the self-diffusion coefficient of ^{125}Sb(III) with increasing tartrate ion concentration indicates formation of a tartrate-Sb(III) complex. Dependence of the self-diffusion of ^{125}Sb(III) on the electrolyte concentration (up to 0·5M) agrees qualitatively with the relation suggested by Onsager, Gosting and Harned.

At a constant ionic strength of the solution the self-diffusion coefficient of a particle changes with its nature (hydrated ion, hydrolysate, polymer, complex)[1-6]. With increasing pH hydrolysis of the ion takes place, hydroxide is formed, and the self--diffusion coefficient decreases[4]. In several papers the dependence between the self-diffusion coefficient and the complex stability constant or association constant was derived, and these constants were calculated from the self-diffusion coefficient values[2,3]. The present paper deals with the dependence of the self-diffusion coefficient of ^{125}Sb(III) on temperature, pH, concentration of complexing agent, and ionic strength of the solution.

EXPERIMENTAL

Apparatus and Procedure

The self-diffusion coefficients of ^{125}Sb(III) were determined with the apparatus suggested by Anderson and Saddington and described in the previous papers[4-6]. The self-diffusion coefficients of each sample were measured simultaneously in five capillaries having constant inner diameter and closed bottom end. Average length of the capillaries was 3·50 cm, inner radius 0·06 cm, volume 0·03 cm^3. The capillaries containing the solution with the radionuclide were immersed in 500 cm^3 inactive solution of the same composition as that of the solution in the capillary and maintained at the temperature 298 ± 0·02 K. Besides these capillaries, three capillaries more were filled with the active solution and were not used for the proper measurement of self-diffusion. These latter capillaries were closed with a rubber stopper at their upper end to prevent evaporation of the solution contained. After the self-diffusion measurement, activity of their solution represented the activity of the solution at the beginning of self-diffusion (A_0) reduced by possible adsorption of the radionuclide on the walls of the capillaries during the self-dif-

fusion measurement. The self-diffusion measurement lasted 95 hours, and after finishing, the solution was pipetted from the capillaries, and its activity (A) was measured. At the same time pH of the inactive solution was measured, too.

Preparation of Solutions, Measurement of Activity and pH

The solutions were prepared from redistilled ($3\times$) water. The initial pH value was adjusted by hydrochloric or nitric acid and sodium hydroxide, pH of the solutions was measured with a glass electrode. The acids and hydroxide used for pH adjusting served also for adjusting of the required ionic strength. The influence of the low electrolyte concentration (about 10^{-6}M) from the radionuclide stock solution on ionic strength of the measured solutions was neglected. The chemicals used for preparation of the solutions were of *p.a.* purity grade. The radionuclide ^{125}Sb(III) did not contain any carrier (product of GDR) and was antimony trichloride chemically. Its gamma activity was measured by a scintillation detector. Inactive Sb(III) was added to ^{125}Sb(III) to make its concentration in the experimental solutions $1 . 10^{-8}$M, $1 . 10^{-5}$M, and $5 . 10^{-5}$M.

Calculation

Values of the self-diffusion coefficients were calculated according to the relation (*1*) previously[4-6], where c_0 and c stand for the initial and the final concentrations of the diffusing ion

$$\frac{c}{c_0} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2\pi^2 Dt}{4h^2}\right), \qquad (1)$$

in the solution in the capillary, respectively, D, h, and t are the self-diffusion coefficient (m^2 s^{-1}), capillary length (m), and time of the self-diffusion measurement (s), respectively.

The concentrations c and c_0 were replaced by radioactivities A and A_0, and the self-diffusion coefficient values were computed with a computer Gier. So many members of Eq. (*1*) were involved in the calculation[6], that the ratio of the last member involved to all preceding ones was $\leq 10^{-6}$. Mean error of the determination of self-diffusion coefficient was calculated as in the previous paper[6], activation energy was calculated from the Arrhenius equation.

RESULTS

Table I gives the self-diffusion coefficients at various pH for $1 . 10^{-8}$M Sb(III) in sodium chloride and nitrate media and for $1 . 10^{-5}$M Sb(III) and $5 . 10^{-5}$M Sb(III) in sodium chloride medium. A marked decrease in the self-diffusion coefficient values of ^{125}Sb(III) was observed at pH 3·5 and 3·6 for the Sb(III) concentrations $1 . 10^{-5}$M and $5 . 10^{-5}$M, respectively.

Table II gives the self-diffusion coefficient values in the temperature range 288 to 298 K for the Sb(III) concentration $1 . 10^{-8}$M at pH 1·5. Table III summarizes the self-diffusion coefficient values of $1 . 10^{-8}$M Sb(III) for various concentrations of the complexing agent — tartrate. At a constant sodium hydroxide concentration (0·1M) the concentrations of chloride and tartrate changed as it is given in Table III.

Dependence of the self-diffusion coefficients of $1 . 10^{-8}$M Sb(III) (pH 2·5) on the electrolyte concentration (NaCl) is illustrated by the following values:

NaCl, M: 0·01   0·1   0·5   1·0   2·0

$D . 10^{10}, m^2 s^{-1}$: 7·43 ± 0·44   7·07 ± 0·57   5·31 ± 0·54   5·63 ± 0·56   6·73 ± 0·59

DISCUSSION

The decrease of the self-diffusion coefficient values with increasing pH (Table I) indicates that a deeper hydrolysis of Sb(III) and formation of its basic salts or possibly hydroxide takes place only in the cases of $1 . 10^{-5}$M Sb(III) and $5 . 10^{-5}$M Sb(III). The maximum hydrolysis and formation of basic salts can be presumed at the lowest value of the self-diffusion coefficient. In the case of $1 . 10^{-8}$M Sb(III) the conditions are less favourable for formation of insoluble hydroxo complexes due to low concentration, and the relative decrease of the self-diffusion coefficient is lower than at $1 . 10^{-5}$ and $5 . 10^{-5}$M Sb(III) concentrations. Certain hydrolysis products of Sb(III) correspond to each pH value and are in equilibrium at this pH. This state is characterized by an average self-diffusion coefficient[2,3] which represents the sum of the self-diffusion coefficients of the individual hydrolysis products (Eq. (2),

TABLE I

pH Dependence of Self-Diffusion Coefficient of ^{125}Sb(III)

Sb(III) M	pH_i	pH_f	$D . 10^{10}$ $m^2 s^{-1}$	Sb(III) M	pH_i	pH_f	$D . 10^{10}$ $m^2 s^{-1}$
$1 . 10^{-8a}$	1·2	1·2	9·66 ± 0·76	$1 . 10^{-5a}$	1·8	1·8	8·11 ± 0·38
	2·5	2·5	7·07 ± 0·57		3·6	3·5	3·54 ± 0·46
	3·5	3·5	7·39 ± 0·30		6·5	6·0	8·01 ± 0·80
	5·5	5·3	7·96 ± 0·33		7·7	7·5	7·08 ± 0·50
	8·5	7·3	7·31 ± 0·52	$5 . 10^{-5a}$	1·4	1·4	7·24 ± 0·71
	10·0	8·1	7·27 ± 0·13		2·0	2·0	6·18 ± 0·70
	11·0	9·1	7·17 ± 0·72		3·6	3·6	2·10 ± 0·21
	12·0	12·0	6·71 ± 0·66		5·6	5·5	7·01 ± 0·15
$1 . 10^{-8b}$	1·4	1·4	8·66 ± 0·21				
	2·5	2·5	6·91 ± 0·20				
	3·6	3·6	8·33 ± 0·41				
	6·2	5·8	8·47 ± 0·20				
	8·3	7·7	7·41 ± 0·34				
	11·4	10·7	6·58 ± 0·14				

[a] Medium of 0·1M-NaCl, [b] medium of 0·1M-NaNO$_3$, pH_i initial pH value, pH_f final pH value.

where D_a stands for the average self-diffusion coefficient of Sb(III), x_i is the proportion of Sb(III) in the i-th state, and D_i means the self-diffusion coefficient of Sb(III) in the i-th state.)

$$D_a = \sum x_i D_i \; . \tag{2}$$

Further increasing of pH results in gradual increase of the self-diffusion coefficient values, soluble anionic hydroxo complexes of Sb(III) are formed. After this transient increase of the self-diffusion coefficients a slow decrease is observed at $1 \cdot 10^{-8}$M Sb(III), if pH is further increased. This decrease could be explained by partial polymerisation of Sb(III) complexes[7,8] resulting in formation of bigger particles whose self-diffusion is slower. Relatively high values of the self-diffusion coefficients of ^{125}Sb(III) in strongly acid medium indicate the presence of the ion SbO^+ besides Sb^{3+}. With respect to the limiting equivalent conductivity of trivalent ions (the respective value of $\frac{1}{3}Sb^{3+}$ was not found in literature, and therefore, the value of the limiting self-diffusion coefficient of Sb^{3+} could not be calculated), the trivalent Sb^{3+}

TABLE II
Temperature Dependence of Self-Diffusion Coefficient of ^{125}Sb(III)
pH 1·5, 0·1M-NaCl, $1 \cdot 10^{-8}$M-Sb(III).

T/K	$D \cdot 10^{10}$, m^2 s^{-1}	dln D/dT
288	2·07 ± 0·09	0·206
293	5·81 ± 0·68	0·067
298	8·11 ± 0·39	

TABLE III
Dependence of Self-Diffusion Coefficient of ^{125}Sb(III) on Tartrate Ion Concentration
$1 \cdot 10^{-8}$M-Sb(III).

$C_4H_4O_6^{2-}$, M	NaCl, M	NaOH, M	$D \cdot 10^{10}$, m^2 s^{-1}
0	0·09	0·01	7·96 ± 0·07
0·04	0·05	0·01	5·59 ± 0·25
0·06	0·03	0·01	4·74 ± 0·37
0·08	0·01	0·01	3·62 ± 0·50
0·09	0	0·01	2·94 ± 0·49

ion should exhibit[9−11] a lower value of the respective self-diffusion coefficient. *E.g.* the self-diffusion coefficient value of trivalent Cr^{3+} in 0·001 molar electrolyte was $0·58 . 10^{-9} m^2 s^{-1}$, whereas the theoretical one (from conductivity of $\frac{1}{3} Cr^{3+}$) was[10] $0·51 . 10^{-9} m^2 s^{-1}$. With Tl^{3+} the limiting value of the self-diffusion coefficient was $0·61 . 10^{-9} m^2 s^{-1}$, and the value determined experimentally in 1M electrolyte[11] was $0·59 . 10^{-9} m^2 s^{-1}$.

Dependence of the self-diffusion of $^{125}Sb(III)$ on temperature is linear within 288 to 298 K (Table II) and fulfils the Arrhenius relation. The calculated activation energy of the self-diffusion of $^{125}Sb(III)$ is 97·4 kJ/mol, *i.e.* higher than that found[12−14] for self-diffusion of NH_4^+, SO_3^{2-} and H_2O. The unusually high temperature coefficient could possibly be explained also by partial hydrolysis of $Sb(III)$ at the both higher temperatures, because $Sb(III)$ shows considerable tendency for hydrolysis[15].

Decrease of the self-diffusion coefficient values of $^{125}Sb(III)$ in Table III is due to formation and gradual increase of $Sb(III)$-tartrate complex concentration with increasing tartrate ion concentration. Course of this dependence testifies stability of chloride complexes of $Sb(III)$, as even at the molar concentration ratio of tartrate to chloride ions 8 : 1 not all $Sb(III)$ was transformed into tartrate complex. The self-diffusion coefficient of $^{125}Sb(III)$ did not reach (at this concentration) the lowest value characterizing the self-diffusion of pure tartrate complex.

Dependence of the self-diffusion coefficient of $^{125}Sb(III)$ on sodium chloride concentration (ionic strength) shows a minimum (see Results) and agrees with analogous dependences found for other ions[16−18]. At low sodium chloride concentrations the self-diffusion coefficient value of $^{125}Sb(III)$ decreases with increasing [NaCl] and agrees qualitatively with the relation suggested by Onsager, Gosting and Harned for self-diffusion of ions in solutions of electrolytes[10,12,16,17]. At the sodium chloride concentrations above 0·5M the self-diffusion coefficient of $^{125}Sb(III)$ began to increase, and its dependence on [NaCl] did not follow the mentioned relation even qualitatively. This discrepancy is explained by viscosity increase and change of dielectric constant of the medium[10,16]. Extrapolation to zero sodium chloride concentration gives a relatively high value of the limiting self-diffusion coefficient of $^{125}Sb(III)$. It could be explained by the presence of SbO^+ besides Sb^{3+} ions, as it was the case with the pH dependence of the $^{125}Sb(III)$ self-diffusion.

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