
Halogenide tin (II) complexes in sulphamate solutions

2. Fluoride complexes

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The dependence of tin electrode potential on KF concentration in acidic sulphamate solutions was investigated by the potentiometric method at temperatures of 25° and 60° and at an ionic strength of the solution 0.6 and 3. Values of concentration stability constants of fluoride tin (II) complexes were calculated by the Leden method.

Key words: Sn (II), complexes, sulphamate solution, temperature, fluoride ions, stability constant

INTRODUCTION

As has been noted in our previous paper [1], the stability constants of tin (II) complexes with both chloride and iodide ions reported in literature differ significantly.

The stability constants and the composition of fluoride tin (II) complexes described in the literature differ even more. Bond and Taylor [2], using the polarographic method, investigated the formation of Sn (II) complexes with F⁻ in an acidic and neutral medium. On the basis of experimental data the authors have concluded that the [SnF]⁺, [SnF₂] and [SnF₃]⁻ complexes are formed independently of the solution pH, while the stability constants depend on the pH. Hence $\beta_1 = 1.2 \cdot 10^4$ l/mol, $\beta_2 = 7 \cdot 10^6$ l²/mol², $\beta_3 = 2.7 \cdot 10^9$ l³/mol³ in an acidic medium and $\beta_1 = 1.0 \cdot 10^4$ l/mol, $\beta_2 = 4.8 \cdot 10^6$ l²/mol², $\beta_3 = 2.9 \cdot 10^9$ l³/mol³ in a neutral medium. The numerical value of the constants is similar, giving grounds to conclude that no mixed tin (II) complexes with OH⁻ and F⁻ ions are formed in the solution. The data of work [3] show that the composition of the complexes depends on the ratio of Sn (II) : F⁻ concentration and complexes with 1–3 F⁻ ions can be formed. Beaudoin Rej and his colleagues [4] have found by means of the potentiometric method that only [SnF]⁺ and [SnF₂] complexes are formed. Small quantities of [SnF₃]⁻ and [SnF₆]²⁻ are formed only at a great excess of HF. However, formation of HF₂⁻ particles is possible in such solutions.

The values of stability constants of Sn (II) complexes with F⁻ ions given in reference books [5–8] differ 100 and more times. The values of constants vary in the ranges: lg K₁ from 4 to 6.26, lg β_2 from 6.85 to 9.16, lg β_3 from 9.43 to 10.96. The different

values of stability constants are conditioned by the different composition, ionic strength and pH of the solutions studied. The value of HF dissociation constant used in calculations may also be of great importance.

In the literature, however, there are very different data on the composition of fluoride tin (II) complexes in the solution. It has been indicated [9, 10] that [SnF₄]²⁻ complexes are formed. A partial formation of such complexes has been also mentioned in [11] where the authors suggest the existence of a NiSnF₄ complex. According to Kohunov and Rakov [12], the complex [SnF₄]²⁻ is formed only conventionally. Authors have proposed that SnF₃⁻ · MeF complexes are formed. The authors also indicate that tin (II) in a strongly acidic medium exists in the form of hydrated ions, even in the presence of F⁻ ions. Solovyeva et al. [13] have noted that [SnF₃OH]²⁻ complexes are formed in the solution when it is alkalinized. Similar results on the formation of such complexes have been also found in [14].

The possibility of the formation of complex compounds Sn (II) with Sn (IV) ions has been also indicated in the paper by Ruchand et al. [15]. Abrahams et al. [16] indicate that a hydrolysis of SnF₂ complexes takes place in concentrated aqueous solutions and Sn₄O₆ oxy complexes are formed.

As can be seen, different authors indicate the possibility of the formation of Sn (II) complexes with F⁻ ions of different composition and stability. Therefore, it is impossible to choose soundly or to calculate the values of the stability constants for the solutions of another ionic composition or temperature. We did not manage to find in the literature

available the stability constants of Sn (II) with fluoride ions in acidic sulphamate solutions.

This work is aimed at determining the composition and concentration stability constants of fluoride Sn(II) complexes depending on the ionic strength and temperature of the solution.

EXPERIMENTAL

Working solutions were prepared and measurements were taken using the methods described in the first part of the work [1].

RESULTS AND DISCUSSION

As has been shown in the first part of our work [1], the tin electrode potential is reversible in relation to Sn (II) ions in a wide range of Sn (II) concentration and can be used as a working electrode during a potentiometric titration. Figures 1 and 2 show the variation of Sn (II) electrode potential when KF is added to the acidic sulphamate solutions. As can be seen from the figures, the tin electrode potential (E_R) shifts to a negative side, independently of the acidity, temperature and ionic strength of electrolyte. It indicates a decrease in the concentration of Sn (II) ions in the solution due to formation of complexes between Sn (II) ions and F^- .

The composition and consecutive concentration stability constants were calculated using the Leden method [1, 17] and the method of "potential deviation" [18]. The method of "potential deviation" [18] is based on an assumption that, predominantly, complexes with the maximum number of ligands are formed in solutions with a great excess of ligand. A linear dependence of $E - \ln(C_L - nC_{Me})$ with a slope nRT/zF (where n is a maximum quantity of ligand in the complex) should be observed here. The deviation potential from the linear dependence is observed in the presence of considerable quantities of the complex with smaller quantities of the ligand MeL_{n-1} . The value of potential deviations is determined by the equation [18]

$$\Delta E = (RT/zF) \cdot \ln \sum \beta_i [L]_i - (RT/zF) \cdot \ln \beta_n - (nRT/zF) \cdot \ln (C_n - nC_{Me}),$$

where all designations are conventional.

When only two complexes, MeL_n and MeL_{n-1} , are present in the solution, it is easy to calculate graphically the equilibrium ligand concentration $[L]$. The value of the calculated stability constant should be constant in a range of negligible potential deviations (2–6 mV).

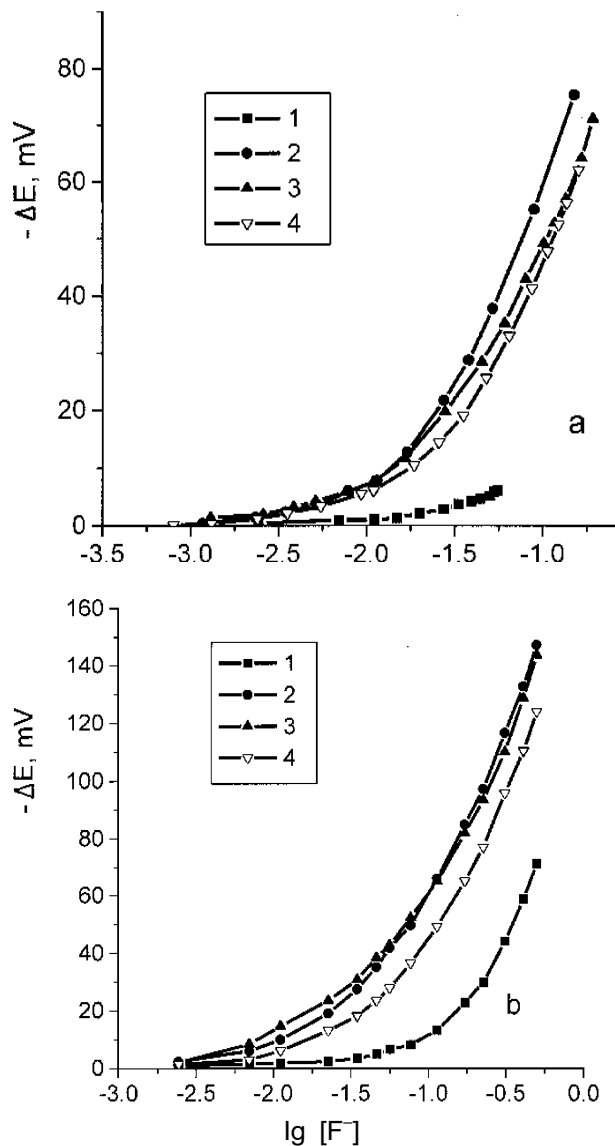


Fig. 1. Dependence of tin electrode potential on KF concentration in solution: Sn (SO₃NH₂)₂ + HSO₃NH₂ + KSO₃NH₂ at μ = 0.6 (a), μ = 3.0 (b), concentration Sn(SO₃NH₂)₂: 1 – 0.1 M; 2, 3 – 0.01 M; 4 – 0.001M, and concentration of HSO₃NH₂: 1, 2 – 0.1M; 3, 4 – 0.25 M. t = 25 °C

Coordination numbers have been calculated by Nernst equation, using the data of Figs. 1 and 2 in a great excess of ligand where the linear dependence $E - \lg i$ is observed and equals to 3.4–4.5. The dependences $E - \ln(C_L - nC_{Me})$ calculated when n is 3 or 4 are linear. The calculated values of stability constants change with the potential within the $\lg \beta$ range 13–9 in both cases. Such an inconsistency of the calculated values means that it is impossible to determine the stability constants in this system by the "potential deviation" method. As has been noted in [18], such inconsistency is possibly due to a

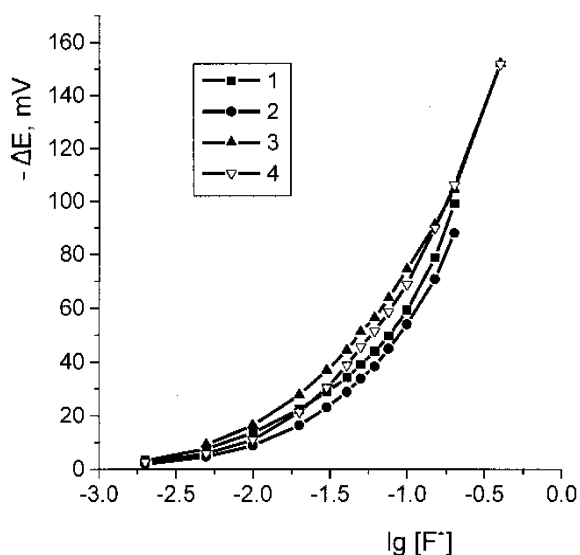


Fig. 2. Dependence of tin electrode potential on KF concentration in solution: $\text{Sn}(\text{SO}_3\text{NH}_2)_2 + \text{HSO}_3\text{NH}_2 + \text{KSO}_3\text{NH}_2$ at $\mu = 0.6$ (1, 2), $\mu = 3.0$ (3, 4), and concentration $\text{Sn}(\text{SO}_3\text{NH}_2)_2$: 1, 3 – 0.001 M; 2, 4 – 0.01 M. $t = 60^\circ\text{C}$

change in the activity coefficient of Sn (II) ions in sulphamate solutions or in the presence of a big number of compounds with a smaller number of the ligand.

Table 1 lists the concentration stability constants of Sn (II) complexes with F^- ions. They have been calculated using the Leden method. In calculations it has been assumed that HSO_3NH_2 and KF dissociate completely and that the dissociation constant

for HF $\text{p}K = 3.208$ [7]. A concentration of hydrogen ions, rather than their activity, has been used in calculations.

It can be seen from the data that $[\text{SnF}]^+$, $[\text{SnF}_2]$ and $[\text{SnF}_3]^-$ ions are formed in the solution, and $[\text{SnF}_3]^-$ complexes are not formed only in solutions with the ionic strength $\mu = 0.6$ and the temperature $t = 60^\circ\text{C}$.

The stability constants of $[\text{SnF}]^+$ and $[\text{SnF}_2]$ complexes are close by their value to those given in the literature [2]. Only the value of the stability constant of $[\text{SnF}_3]^-$ complex is higher. Such a discrepancy may be explained by the fact that the authors assumed that the dissociation constant of HF is equal to $\text{p}K 2.573$.

A distribution of Sn (II) among separate complexes as a function of the total ligand concentration in the electrolyte has been calculated on the basis of an averaged consecutive stability constants of tin (II) fluoride complexes. Their values are given in Table 1.

In the calculations, it has been taken into account that hydroxocomplexes may be present in acidic solutions. The stability constants are equal to ($\text{p}\beta$) $\text{SnOH}^+ 11.6$, $\text{Sn}(\text{OH})_2 - 9.31$, $\text{Sn}(\text{OH})_3^- - 4.45$ [7]. Figures 3 and 4 present the obtained results. Only the complexes whose concentration exceeds 0.1% from the total one are shown in Fig. 3 and 4. As can be seen from the figures, hydroxocomplexes may also be present alongside fluoride complexes of Sn (II) in acidic sulphamate solutions. When calculating the stability constants of fluoride complexes,

Table 1. $\lg\beta$ of consecutive stability constants of fluoride Sn (II) complexes depending on composition of sulphamate electrolyte and temperature

Ionic strength of solution	Temperature, $^\circ\text{C}$	C HSO_3NH_2 , M	Complex	C $\text{Sn}(\text{SO}_3\text{NH}_2)_2$, M		
				0.001	0.01	0.1
0.6	25	0.10	SnF^+		4.07 ± 0.05	3.30 ± 0.05
			SnF_2		8.54 ± 0.06	
			SnF_3^-		12.50 ± 0.10	
0.6	25	0.25	SnF^+	4.42 ± 0.05	4.03 ± 0.05	
			SnF_2	8.59 ± 0.06	8.36 ± 0.06	
			SnF_3^-	12.20 ± 0.10	12.95 ± 0.10	
3.0	25	0.10	SnF^+		4.56 ± 0.05	
			SnF_2		8.44 ± 0.06	
			SnF_3^-		12.50 ± 0.10	
3.0	25	0.25	SnF^+	4.31 ± 0.05	4.28 ± 0.05	3.75 ± 0.05
			SnF_2	9.40 ± 0.06	9.20 ± 0.06	8.48 ± 0.06
			SnF_3^-	12.97 ± 0.10	12.74 ± 0.10	
0.6	60	0.10	SnF^+	4.34 ± 0.05	4.11 ± 0.05	
			SnF_2	8.20 ± 0.10	8.20 ± 0.10	
3.0	60	0.10	SnF^+	4.46 ± 0.05	4.24 ± 0.05	
			SnF_2	8.33 ± 0.06	8.70 ± 0.10	
			SnF_3^-	11.45 ± 0.10		

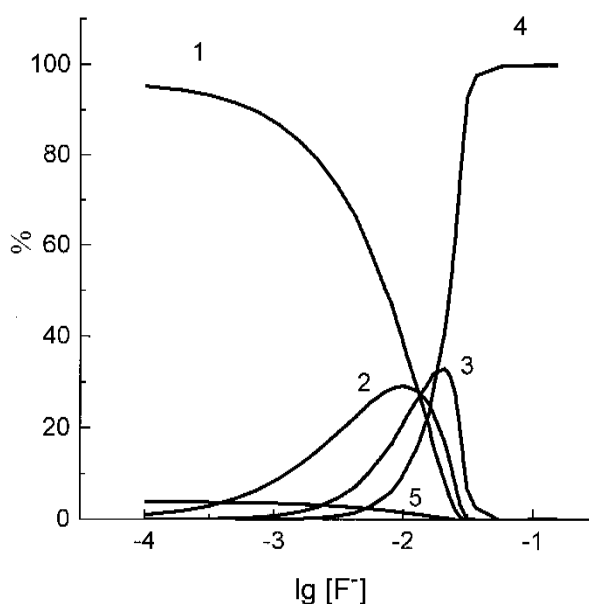


Fig. 3. The degree of formation of tin (II) complexes depending on the concentration of fluoride ions in solutions with the total concentration of Sn (II) 0.01M, $\mu = 0.6$. Curves: 1 - Sn (II), 2 - SnF⁺, 3 - SnF₂, 4 - SnF₃⁻, 5 - Sn(OH)⁺. $t = 25$ °C. pH = 1

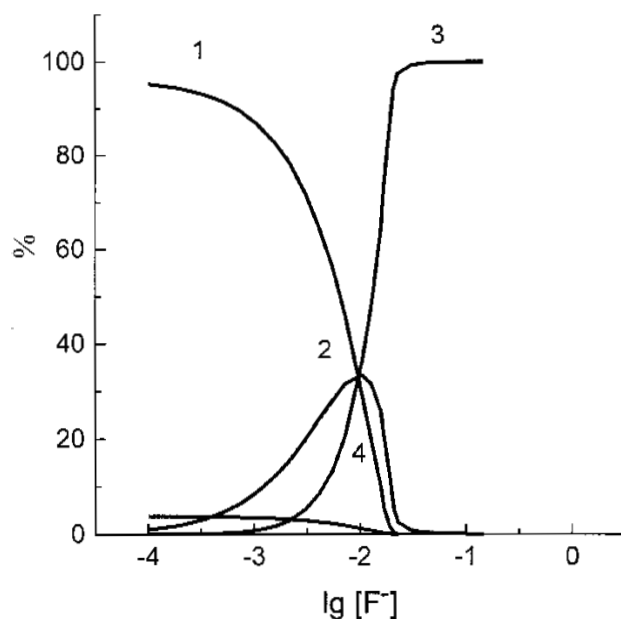


Fig. 4. The degree of formation of tin (II) complexes depending on the concentration of fluoride ions in solutions with the total concentration of Sn (II) 0.01 M, $\mu = 0.6$. Curves: 1 - Sn (II), 2 - SnF⁺, 3 - SnF₂, 4 - Sn(OH)⁺. $t = 60$ °C. pH = 1

the concentration of hydroxocomplexes has not been taken into account. This is not very important when calculating the stability constants using the Leden method, and it may considerably affect the results of calculations obtained by the method of "potential deviation".

CONCLUSIONS

Concentration consecutive stability constants of fluoride tin (II) complexes have been determined depending on the composition and temperature of acidic sulphamate solutions. They are equal to:

$$\lg K = 4.26 \pm 0.05, \lg \beta_2 = 8.50 \pm 0.06, \lg \beta_3 = 12.55 \pm 0.10, (\mu = 0.6, t = 25 \text{ }^\circ\text{C})$$

$$\lg K = 4.19 \pm 0.05, \lg \beta_2 = 8.30 \pm 0.06, (\mu = 0.6, t = 60 \text{ }^\circ\text{C})$$

$$\lg K = 4.28 \pm 0.05, \lg \beta_2 = 9.00 \pm 0.06, \lg \beta_3 = 12.74 \pm 0.10, (\mu = 3.0, t = 25 \text{ }^\circ\text{C})$$

$$\lg K = 4.35 \pm 0.05, \lg \beta_2 = 8.54 \pm 0.06, \lg \beta_3 = 11.45 \pm 0.10, (\mu = 3.0, t = 60 \text{ }^\circ\text{C}).$$

Received
2 November 1999

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**HALOGENIDINIAI ALAVO (II) KOMPLEKSAI
SULFAMO TIRPALUOSE
2. FLUORIDINIAI KOMPLEKSAI**

S a n t r a u k a

Ištirta alavo elektrodo potencialo priklausomybė rūgščiuose sulfamo tirpaluose potenciometrinio titravimo metodu nuo KF koncentracijos 25 ir 60°C temperatūrose. Eksperimentinių duomenų pagrindu Ledeno metodu apskaičiuotos pakopinės koncentracinės patvarumo konstantos 25 ir 60°C temperatūrose.

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**ГАЛОГЕНИДНЫЕ КОМПЛЕКСЫ ОЛОВА (II) В
СУЛЬФАМИНОВЫХ РАСТВОРАХ
2. ФТОРИДНЫЕ КОМПЛЕКСЫ**

Р е з ю м е

Исследована зависимость потенциала оловянного электрода в кислых растворах в зависимости от концентрации KF потенциометрическим методом при температуре 25 и 60 °С. На основе экспериментальных данных, методом Ледена, рассчитаны значения ступеньчатых констант устойчивости фторидных комплексов олова(II) при температуре 25 и 60 °С.