COLLOIDAL CHEMISTRY
AND ELECTROCHEMISTRY

Calculating Equilibrium Constants in the SnCl₂−H₂O−NaOH System According to Potentiometric Titration Data

L. N. Maskaeva[a,b], E. A. Fedorova[a,*], R. A. Yusupov[c], and V. F. Markov[a,b]

[a] Ural Federal University, Yekaterinburg, 620075 Russia
[b] Ural Institute of State Fire Service of EMERCOM of Russia, Yekaterinburg, 620062 Russia
[c] Kazan National Research Technological University, Kazan, 420015 Russia
***e-mail: ka_fed-ra@mail.ru**
Received July 3, 2017

Abstract—The potentiometric titration of tin chloride $SnCl_2$ is performed in the concentration range of 0.00009−1.1 mol/L with a solution of sodium hydroxide NaOH. According to potentiometric titration data based on modeling equilibria in the $SnCl_2−H_2O−NaOH$ system, basic equations are generated for the main processes, and instability constants are calculated for the resulting hydroxo complexes and equilibrium constants of low-soluble tin(II) compounds. The data will be of interest for specialists in the field of theory of solutions.

INTRODUCTION

Semiconductor compounds of tin, such as sulfide SnS, selenide SnSe, and oxide SnO_2 in thin-film state are promising materials in different fields of modern electronics, namely, holographic recording [1, 2], the detection of IR radiation [3], infrared memory devices [3–6], and in the design of sensors, lasers, thermoelectric elements [2, 6–13], and photovoltaic devices [14–17].

To prepare single-phase layers of SnS and SnSe, vacuum [18–22] and vapor-phase technologies [23–25], which require complex equipment, are widely employed, along with simpler liquid-phase methods, especially chemical precipitation from aqueous solutions [2, 26–33]. It should be noted that the synthesis of thin films of SnS, SnSe, SnO_2 via hydrochemical technology is complicated, due to the hydrolysis of tin(II) salts in bulk solution [34–38] with the formation of tin(II) hydroxide, which is characterized by a very low solubility product (6.3×10^{-27} [39]).

The results from studies aimed at investigating the ionic state of tin(II) in aqueous solutions, are quite contradictory. According to [35], the formation of complex forms of tin is possible ($SnOH^+$, $Sn_2(OH)_2^{2+}$, and $Sn_3(OH)_4^{2+}$), while it was suggested in [38] that binuclear complex $Sn_2(OH)_3^+$ can be present in a solution. The authors in this case rejected the possible formation of mononuclear ions of $SnOH^+$. In [36], a basic series of hydroxo forms with coordination numbers of 1 to 3 was discussed along with the abovementioned metal complexes, along with the formation of the barely soluble compound $Sn(OH)_{2(S)}$. These scattered and contradictory data indicate a need for further studies aimed at obtaining more reliable data on the formation of hydroxo complexes and low-soluble tin(II) compounds in aqueous solutions and determining their stability constants.

The formation of a theoretically rationalized basis for the targeted synthesis of tin(II) sulfide and selenide is helped by the potentiometric titration of tin chloride solutions with sodium hydroxide using the original procedure given in [40] for processing the results.

The aim of this work was thus to investigate equilibria in the system $SnCl_2−H_2O−NaOH$ via mathematical modeling of the results from potentiometric titration to determine the equilibrium constants and conditions of the formation of hydroxo complexes in solution and low-soluble tin(II) compounds.

EXPERIMENTAL

An experimental data set for the potentiometric titration of tin chloride $SnCl_2$ solutions with concentrations of 0.00009 to 1.1 mol/L using sodium hydroxide was obtained. The concentration of NaOH was 0.001−10.05 mol/L.
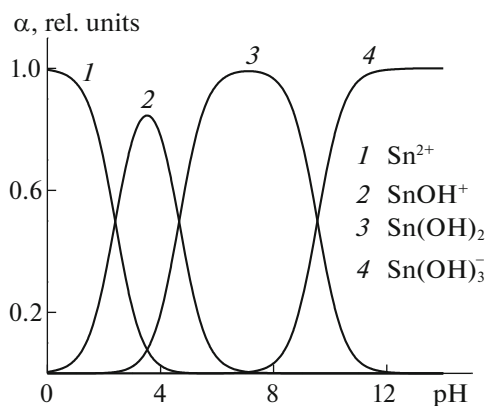
Fig. 1. Diagram of the distribution of some concentrations of Sn^{2+} ions and mononuclear tin(II) hydroxo complexes in the $Sn^{2+}-H_2O-OH^-$ system vs. the pH of the medium at total analytical concentration of tin $C^{\Sigma}_{Sn(II)} = 0.03$ mol/L and $T = 298$ K.

Experiments were conducted according to the standard procedure: a particular volume of tin salt solution with known concentration was introduced into a glass beaker to which a titrated solution of sodium hydroxide was added dropwise from a burette with stirring using a magnetic stirrer. At the end of each interval between drops of 30 to 180 s, the added volume of alkali and corresponding pH of the salt solution were recorded.

The results from titration were processed using EQ-5 program package described in [40].

RESULTS AND DISCUSSION

Let us first examine the ionic equilibria that arise in the system $Sn^{2+}-H_2O-OH^-$ by considering only mononuclear metal hydroxo complexes. We used the computational approach proposed in [41] to determine the fraction of uncomplexed tin(II) ions along with all complex compounds in this system.

Figure 1 presents the dependence of the fractional concentrations of free ions and Sn (II) hydroxo complexes in the system $Sn^{2+}-H_2O-OH^-$, which are characterized by the instability constants [39] $pk_{inst1}(SnOH^+) = 11.60$, $pk_{inst2}(Sn(OH)_2) = 20.94$, and $pk_{inst3}(Sn(OH)_3^-) = 25.39$, depending on the pH of the medium.

Hydrolysis starts with the formation of mononuclear ion $SnOH^+$, whose fraction in solution at pH ≈ 3.5 is ~0.85. The range of existence of the molecular form of $Sn(OH)_2$ agrees with the literature data on pH, from ~2.0 to the complete precipitation of hydroxide at 4.7—10.0 [34, 39]. At pH > 10, almost all tin(II) (more than 99%) in the solution exists in the

form of complex ions of $Sn(OH)_3^-$, the product of the hydrolytic process with the participation of previously formed metal hydroxide.

Analysis of the ionic equilibria in the system $Sn^{2+}-H_2O-OH^-$ thus proves the ability of tin(II) compounds to hydrolyze, which starts with the formation of mononuclear hydroxo complex with a coordination number of 1. In the broad range of pH 5.0—9.5, metal in the form of neutral particles of $Sn(OH)_2$ predominates. In a strongly alkaline medium, stannate ion $Sn(OH)_3^-$ is formed at pH > 10, due to the hydrolytic decomposition of tin(II) hydroxide.

Despite the relevance of the problem, there are few works on investigating equilibria in the system $SnCl_2-H_2O-NaOH$, and the results are quite contradictory. For example, it is known [35] that when diluting $SnCl_2$ solution with water, it becomes turbid because of the formation of barely soluble basic salt SnOHCl [35, 36, 42, 43], but during the titration of tin(II) chloride solution with alkali a precipitate forms whose composition during titration varies from $Sn(OH)_{0.67}Cl_{1.33}$ to $Sn(OH)_{1.86}Cl_{0.14}$. The authors of [35] believed these compounds exist in the system at a slight deviation from equilibrium, since only basic tin(II) chloride with a composition of $3SnOSnCl_2 \cdot 3H_2O$ $(Sn(OH)_{1.5}Cl_{0.5} \cdot 0.75H_2O)$ was isolated from chloride aqueous solutions. The statement that all compositions of the resulting barely soluble compounds in the system $Sn^{2+}-H_2O-OH^-$ differ by minimum nuclearity (i.e., they are mononuclear) is, in our opinion, not correct.

During hydrolysis, the probability of polynuclear tin(II) hydroxo complexes emerging is quite high. One example is that in works devoted to the potentiometric titration of tin(II) sulfate with alkali, the formation of solid-phase compounds of the below compositions was determined by modeling the equilibria in the system: $Sn(OH)_{2(S)}$, $Sn_2(OH)_2SO_{4(S)}$, $Sn_4(OH)_6SO_{4(S)}$, $Sn_8(OH)_{14}SO_{4(S)}$, and $SnO_{(S)}$ [44—46]. Most of these are complex polynuclear formations. Assuming this is true, it is of practical importancr to investigate the equilibria that arise in solutions of tin chloride $SnCl_2-H_2O-NaOH$. Determining the composition and ranges of existence of complex forms and tin(II) compounds in a solution is necessary in order to predict the concentration boundaries of the formation and further optimization of hydrochemical synthesis of tin(II) sulfide and selenide films when using its chloride salt.

The results from the potentiometric titration of 0.00009—1.1 M $SnCl_2$ solutions with 0.001—10.05 mol/L NaOH are presented in Fig. 2 in coordinates $n_{OH^-} = f(pH)$. The authors of [37] noted that solutions of tin(II) salts are quickly oxidized with
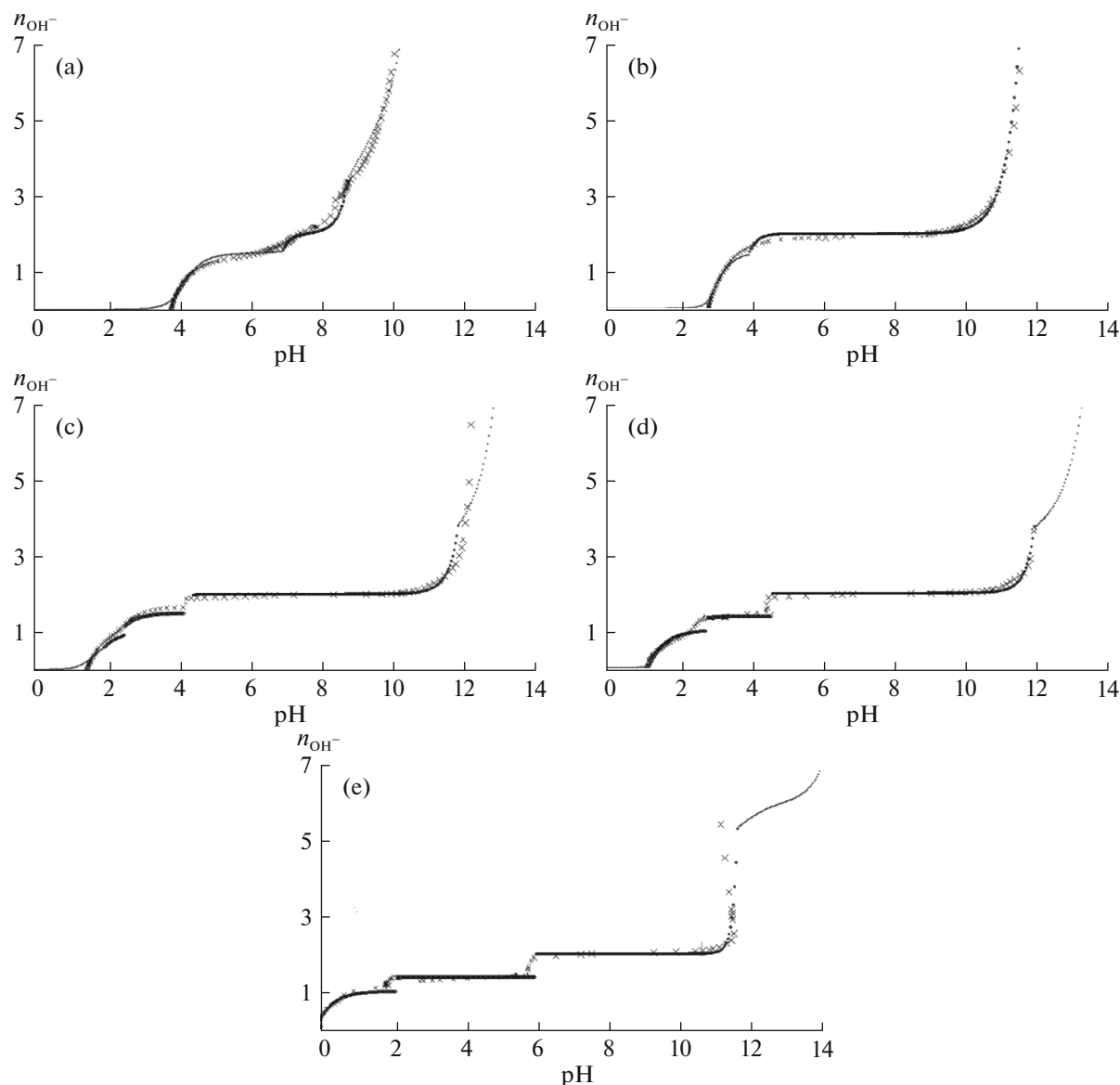
Fig. 2. Dependences of the function of formation on hydroxide ion n_{OH^-} on the pH of SnCl$_2$ solutions, according to the results from processing experimental (crosses) and theoretical (bold lines) curves of the potentiometric titration of tin(II) salt with sodium hydroxide at the following initial concentrations of components, mol/L: (a) $C_{Sn(II)} = 0.00009$, $C_{NaOH} = 0.001$; (b) $C_{Sn(II)} = 0.0008$, $C_{NaOH} = 0.01$; (c) $C_{Sn(II)} = 0.03$, $C_{NaOH} = 0.30$; (d) $C_{Sn(II)} = 0.12$, $C_{NaOH} = 0.98$; and (e) $C_{Sn(II)} = 1.10$, $C_{NaOH} = 10.20$; $T = 25°$C.

atmospheric oxygen, so freshly prepared solutions of chloride SnCl$_2$ were used to avoid this process.

More complete hydrolysis of tin salt solution SnCl$_2$ with an increase in its concentration from 0.00009 to 1.10 mol/L is indicated by the shift of pH of the start of potentiometric titration curves from 3.8 to 0 (Fig. 2).

The function of formation of metal ion, which determines the number of atoms of complexing agent (Sn^{2+} ions) on one molecule of compound was evaluated from the slope at the start of the step on the curve; the higher the slope of potentiometric titration curve

or the lower the slope, the higher the function of formation on a metal ion [47]. The slope of curve $n_{OH^-} = f$(pH) does not change up to the content of tin(II) chloride of 0.0008 mol/L (Figs. 2a, 2b). However, raising the initial concentration of SnCl$_2$ in solution up to 0.03 mol/L lowers the slope of the potentiometric titration curve (Fig. 2c), due presumably to the simultaneous formation of polynuclear complexes and barely soluble metal compounds. At the maximum concentration of SnCl$_2$ corresponding to 1.10 mol/L, there is in fact a straightening of the initial section of

the curve (Fig. 2e), due presumably to a reduction in the number of complex forms of Sn(II).

By projecting the plateau on the ordinate axis that characterizes the function of formation on OH$^-$ ions, we can estimate the composition of the solid-phase metal compounds. The value of this function is 2 over the range of tin salt concentrations in the system SnCl$_2$–H$_2$O–NaOH, which corresponds to the formation of a phase with the stoichiometric composition Sn(OH)$_{2x(S)}$.

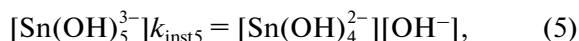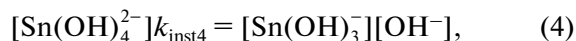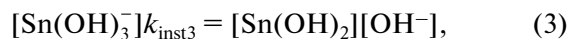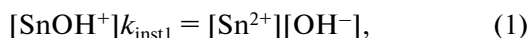At a content of tin chloride SnCl$_2$ corresponding to 0.00009 mol/L (Fig. 2a), the formation of the above-mentioned barely soluble compound is possible in the fairly narrow pH range of 7 to 8, as is indicated by the broad line modeled according to the results from potentiometric titration.

Raising the initial concentration of metal salt in the considered system to 0.12 mol/L (Fig. 2d) considerably extends the range of existence of the phase Sn(OH)$_{2x(S)}$ in the interval of pH 4.5–12.1. At [SnCl$_2$] = 1.10 mol/L, however, the pH range in which this compound can be isolated is again limited to 5.9–11.7.

In all of the potentiometric titration curves, a step can be observed with function of formation n_{OH^-} = 1.5; at salt contents of up to 0.0008 mol/L (Figs. 2a, 2b), this is indicated in the figure by a thin line suggesting that the formation of solid phase with the formula composition Sn$_x$(OH)$_{1.5x}$Cl$_{0.5x(S)}$ does not occur under these conditions. However, the fractional concentration of the corresponding polynuclear hydroxo complex Sn$_x$(OH)$_{1.5x}^{(2x-1.5x)+}$ greatly exceeds the content of other complex forms and compounds of tin(II) in the solution. A further increase in the concentration of SnCl$_2$ in solution yields a barely soluble compound with a stoichiometric composition of Sn$_x$(OH)$_{1.5x}$Cl$_{0.5x(S)}$. Its range of existence lies within $2.3 \leq$ pH ≤ 4.4 at a concentration of SnCl$_2$ = 0.03 mol/L and varies up to pH 1.9–5.9 at the maximum concentration of tin(II) salt corresponding to 1.10 mol/L (Fig. 2e).

At concentrations of tin chloride higher than 0.03 mol/L (Fig. 2c) in acidic media (pH < 2.4), we observe an additional step on the potentiometric titration curves with the function of formation on hydroxide ion n_{OH^-} = 1, confirming the isolation of primarily solid phase Sn$_x$(OH)$_x$Cl$_{x(S)}$ from the solution. Only after that is the formation of a weakly soluble compound with the composition Sn$_x$(OH)$_{1.5x}$Cl$_{0.5x(S)}$ possible.

Using the results from computer modeling of the main equilibrium processes in the system SnCl$_2$–H$_2$O–NaOH during potentiometric titration, we generated the corresponding equations:

$$[SnOH^+]k_{inst1} = [Sn^{2+}][OH^-], \qquad (1)$$

$$[Sn(OH)_2]k_{inst2} = [SnOH^+][OH^-], \qquad (2)$$

$$[Sn(OH)_3^-]k_{inst3} = [Sn(OH)_2][OH^-], \qquad (3)$$

$$[Sn(OH)_4^{2-}]k_{inst4} = [Sn(OH)_3^-][OH^-], \qquad (4)$$

$$[Sn(OH)_5^{3-}]k_{inst5} = [Sn(OH)_4^{2-}][OH^-], \qquad (5)$$

$$[Sn(OH)_6^{4-}]k_{inst6} = [Sn(OH)_5^{3-}][OH^-], \qquad (6)$$

$$[Sn_2(OH)_2^{2+}]k_{inst7} = [Sn(OH)^+]^2, \qquad (7)$$

$$[Sn_4(OH)_6^{2+}]k_{inst8} = [Sn(OH)^+]^2[Sn(OH)_2]^2, \qquad (8)$$
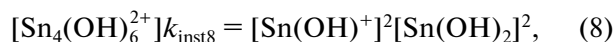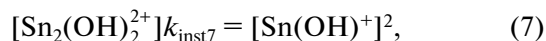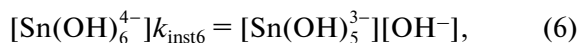
where k_{inst1}–k_{inst8} are the equilibrium constants of the corresponding processes that characterize the stability of the inner sphere of complex ions or instability constants.

It was noted earlier that the formation of different mono- and polynuclear barely soluble compounds in the considered system is possible: these include Sn(OH)$_{2S}$ (k_{inst2S}), Sn$_2$(OH)$_2$Cl$_{2S}$ (k_{inst7S}), and Sn$_4$(OH)$_6$Cl$_{2S}$ (k_{inst8S}), where k_{inst2S}, k_{inst7S}–k_{inst8S} are the equilibrium constants of the formation of corresponding solid phases.

Table 1 presents the instability constants of processes (1)–(8) for systems SnCl$_2$–H$_2$O–NaOH and SnSO$_4$–H$_2$O–NaOH, calculated using the results from potentiometric titration and the known reference data. The instability constants we calculated for the first three tin(II) complex ions given in a basic series agree with the values given in reference literature. However, there is a slight divergence of the exponents of constants, which were obtained using the results from mathematical modeling for the systems with tin

Table 1. Instability constants of hydroxo complexes and equilibrium constants of low-soluble tin(II) compounds calculate using potentiometric titration data of tin chloride with sodium hydroxide. Calculated values of corresponding parameters are given for comparison for the system SnSO$_4$–H$_2$O–NaOH using the data from [46] (II) and reference values from [39] (III)

Parameters	I	II	III
pk_{inst1}	9.6 ± 0.3	10.60	11.60
pk_{inst2}	18.7 ± 0.5	21.10	20.94
pk_{inst3}	24.4 ± 0.8	25.55	25.39
pk_{inst4}	28.5 ± 0.6	29.35	—
pk_{inst5}	31.4 ± 0.3	32.65	—
pk_{inst6}	31.7 ± 0.7	35.85	—
pk_{inst7}	6.6 ± 0.1	5.65	—
pk_{inst8}	18.5 ± 0.5	19.0	—
pk_{inst2S}	−5.7 ± 0.4	—	—
pk_{inst7S}	−4.5 ± 0.2	—	—
pk_{inst8S}	−1.9 ± 0.9	—	—
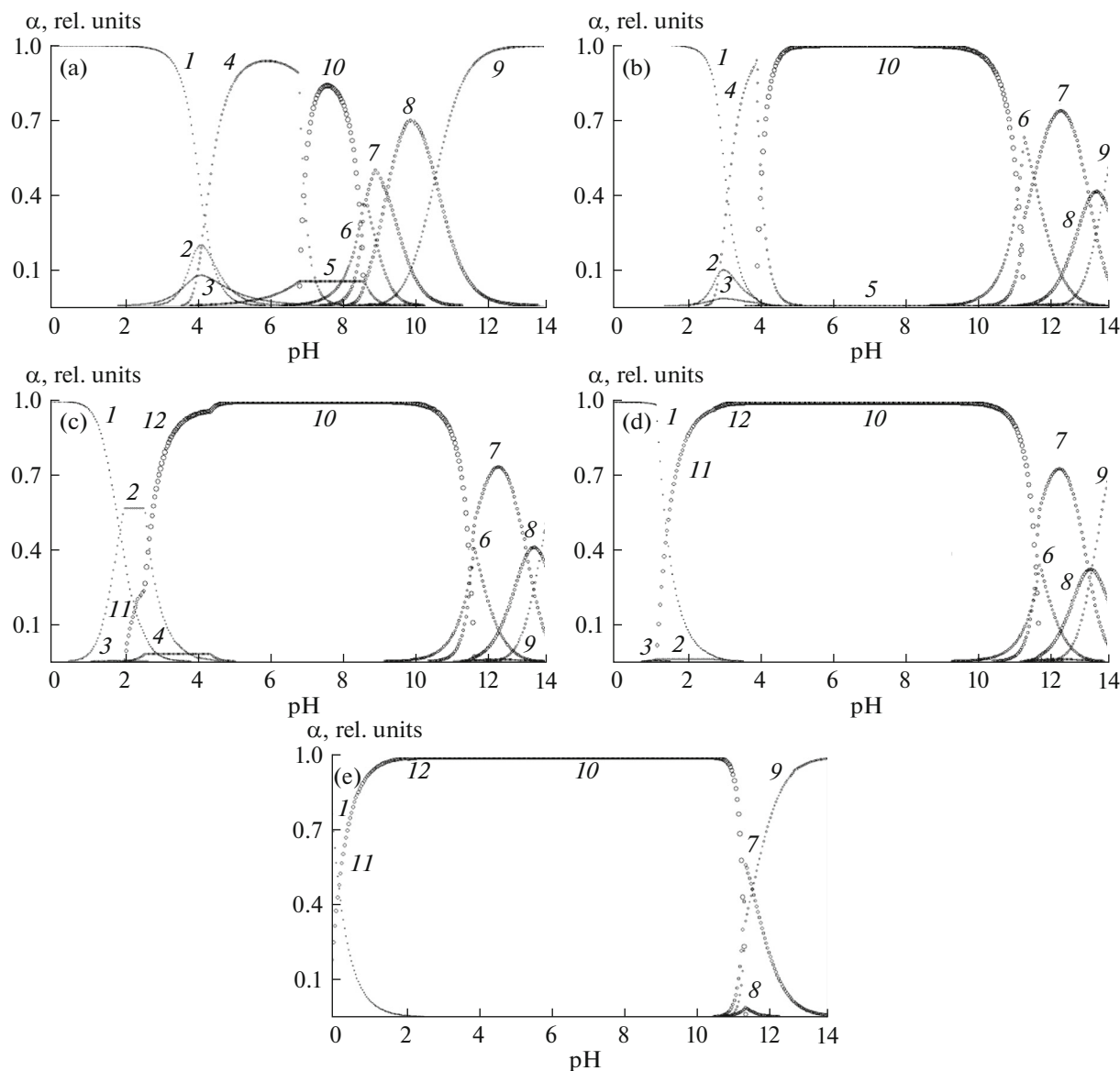
Fig. 3. Calculated overlapping ranges of (*1*) the existence of Sn^{2+} ions and formation of hydroxo complexes (*2*) Sn$_2$(OH)$_2^{2+}$, (*3*) SnOH$^+$, (*4*) Sn$_4$(OH)$_6^{2+}$, (*5*) Sn(OH)$_2$, (*6*) Sn(OH)$_3^-$, (*7*) Sn(OH)$_4^{2-}$, (*8*) Sn(OH)$_5^{3-}$, and (*9*) Sn(OH)$_6^{4-}$ plus low-soluble compounds (*10*) Sn(OH)$_{2S}$, (*11*) Sn$_2$(OH)$_2$Cl$_{2S}$, and (*12*) Sn$_4$(OH)$_6$Cl$_{2S}$ in aqueous solutions of SnCl$_2$ at the following initial concentrations of tin(II) chloride and sodium hydroxide, mol/L: (a) $C_{Sn(II)} = 0.00009$, $C_{NaOH} = 0.001$; (b) $C_{Sn(II)} = 0.0008$, $C_{NaOH} = 0.01$; (c) $C_{Sn(II)} = 0.03$, $C_{NaOH} = 0.30$; (d) $C_{Sn(II)} = 0.12$, $C_{NaOH} = 0.98$; and (e) $C_{Sn(II)} = 1.10$, $C_{NaOH} = 10.20$; $T = 25°C$.

chloride and sulfate. This could be due to either the nature of the metal salt anion, the conditions of preparing or storing the titrated solutions, or the conducting of potentiometric titration.

The shared distribution of complex forms and low-soluble tin(II) compounds formed in the system SnCl$_2$–H$_2$O–NaOH depending on pH at different initial concentrations of the reagents is given in Fig. 3.

The possibility was noted above of the formation of just mononuclear barely soluble tin(II) compound

with the formula composition Sn(OH)$_{2x(S)}$ at a concentration of metal salt in the analyzed solution of 0.00009 mol/L (Fig. 2a). In Fig. 3a, which presents the calculated ranges of the formation of various complex forms of tin and its low-soluble compounds, we can see that this phase corresponds to hydroxide Sn(OH)$_{2(S)}$. The complex ion with function of formation $n_{OH^-} = 1.5$ in turn corresponds to composition Sn$_4$(OH)$_6^{2+}$. Along with these complex forms of Sn(II), the formation of a full basic series of hydroxo

complexes with coordination numbers of 1 to 6, along with polynuclear $Sn_2(OH)_2^{2+}$, is possible. As shown above, raising the concentration of $SnCl_2$ to 0.0008 mol/L (Fig. 3b) extends the pH range of existence of metal hydroxide from 4.4 to 11.7, and the formation of barely soluble compounds of different composition is not observed.

As follows from Figs. 3c−3e, compounds with compositions $Sn_x(OH)_xCl_{x(S)}$ and $Sn_x(OH)_{1.5x}Cl_{0.5x(S)}$ form in a solution of tin(II) chloride in the 0.03 to 1.10 mol/L range of concentrations, depending on the pH and the mononuclear solid-phase compound in the relatively acidic medium. A barely soluble phase of $Sn_2(OH)_2Cl_{2(S)}$ forms at pH < 2.4 in particular, while polynuclear compound $Sn_4(OH)_6Cl_{2(S)}$ forms at higher values of pH ≈2.4−4.4. In a strongly basic medium at pH > 11, complete hydrolytic cleavage of the precipitates occurs with the formation of tin hydroxo complexes $Sn(OH)_3^-$, $Sn(OH)_4^{2-}$, $Sn(OH)_5^{3-}$, and $Sn(OH)_6^{4-}$.

CONCLUSIONS

Potentiometric titration of tin chloride $SnCl_2$ solutions with a concentration of 0.00009−1.1 M with sodium hydroxide NaOH 0.001−10.05 mol/L showed that an increase in the content of salt ensures its more complete hydrolysis, plus an increase in the amount of polynuclear hydroxo complexes and low-soluble compounds with a drop in their number at the maximum concentration of metal salt and alkali. Instability constants of tin(II) hydroxo complexes and equilibrium constants of the resulting low-soluble metal compounds, calculated from the results of the conducted potentiometric titration, can be recommended as reference values.

ACKNOWLEDGMENTS

REFERENCES

1. A. Yu. Betin, V. I. Bobrinev, N. N. Evtikhiev, et al., Appl. Opt. **52**, 8142 (2013).

2. V. R. Solanki, R. J. Parmar, R. J. Pathak, and M. D. Parmar, in *Proc. of the International Conference on Functional Oxides and Nanomaterials,* AIP Conf. Proc. **1837**, 040019-1 (2017).

3. M. S. Mahdi, K. Ibrahim, A. Hmood, et al., RSC Adv. **116**, 114980 (2016).

4. D. Avellaneda, G. Delgado, M. T. S. Nair, and P. K. Nair, Thin Solid Films **515**, 5771 (2007).

5. Z. Zainal, S. Nagalingam, A. Kassim, et al., Solar Energy Mater. Solar Cells **81**, 261 (2004).

6. K. Zweibel, Solar Energy Mater. Solar Cells **63**, 375 (2000).

7. N. Lindgren, M. Larsson, and S. Lindquist, Solar Energy Mater. Solar Cells **73**, 377 (2002).

8. J. B. Johnson, H. Jones, B. S. Latham, et al., Semicond. Sci. Technol. **14**, 501 (1999).

9. T. Jiang, G. A. Ozin, A. Verma, and R. L. Bedard, J. Mater. Chem. **8**, 1649 (1998).

10. M. Batzill and U. Diebold, Prog. Surf. Sci. **79**, 47 (2005).

11. S. A. Pianaro, P. R. Bueno, E. Longo, and J. A. Varela, J. Mater. Sci. Lett. **14**, 692 (1995).

12. V. E. Bochenkov and G. B. Sergeev, Russ. Chem. Rev. **76**, 1013 (2007).

13. A. Ammari, B. Bellal, N. Zebbar, et al., Thin Solid Films **632**, 66 (2017).

14. S. A. Bashkirov, V. F. Gremenok, and V. A. Ivanov, Semiconductors **45**, 749 (2011).

15. K. T. R. Reddy, N. K. Reddy, and R. W. Miles, Solar Energy Mater. Solar Cells **90**, 3041 (2006).

16. M. Sharon and K. Basavaswaran, Solar Cells **25**, 97 (1988).

17. M. Gunasekaran and M. Ichimura, Solar Energy Mater. Solar Cells **91**, 774 (2007).

18. L. S. Parshina, O. D. Khramova, O. A. Novodvorsky, A. A. Lotin, I. A. Petukhov, F. N. Putilin, and K. D. Shcherbachev, Semiconductors **51**, 407 (2017).

19. C. Cifuentes, M. Botero, E. Romero, et al., Brazil. J. Phys. **36** (3B), 1046 (2006).

20. M. Devika, N. K. Reddy, F. Patolsky, and K. R. Gunasekhar, J. Appl. Phys. **104**, 124503 (2008).

21. S. A. Bashkirov, V. F. Gremenok, V. A. Ivanov, and V. V. Shevtsova, Phys. Solid State **54**, 2497 (2012).

22. B. Stjerna, E. Olsson, and C. G. Granqvist, J. Appl. Phys. **76**, 3797 (1994).

23. J. Park, M. Song, W. M. Jung, et al., Bull. Korean Chem. Soc. **33**, 3383 (2012).

24. P. Sinsermsuksakul, K. Hartman, S. B. Kim, et al., Appl. Phys. Lett. **102**, 053901 (2013).

25. V. S. Popov, V. G. Sevast'yanov, and N. T. Kuznetsov, Kompoz. Nanostrukt., No. 1, 33 (2012).

26. L. N. Maskaeva, E. A. Fedorova, V. F. Markov, et al., Butler. Soobshch. **37** (2), 1 (2014).

27. L. N. Maskaeva, S. S. Tulenin, A. A. Timina, and V. F. Markov, Butler. Soobshch. **45** (3), 72 (2016).

28. S. S. Tulenin, A. A. Timina, L. N. Maskaeva, and V. F. Markov, Russ. J. Appl. Chem. **90**, 91 (2017).

29. L. P. Joshi, L. Risal, and S. P. Shrestha, J. Nepal Phys. Soc. **3**, 1 (2015).

30. S. H. Chaki, M. D. Chaudhary, and M. P. Deshpande, J. Semicond. **37**, 053001(2016).

31. O. D. Nnanyere, J. Nat. Sci. Res. **5**, 124 (2015).

32. M. Safonova, E. Mellikov, V. Mikli, et al., Adv. Mater. Res. **1117**, 183 (2015).

33. T. N. Fetisova, V. R. Mirolyubov, and S. F. Katyshev, Russ. J. Gen. Chem. **77**, 1643 (2007).

34. V. A. Nazarenko, V. P. Antonovich, and E. M. Nevskaya, *The Hydrolysis of Metal Ions in Diluted Solutions* (Atomizdat, Moscow, 1979) [in Russian].

35. V. B. Spivakovskii, *Analytical Chemistry of Tin* (Nauka, Moscow, 1975) [in Russian].

36. R. M. Cigala, F. Crea, C. de Stefano, et al., Monatsh. Chem. **144**, 761 (2013).

37. O. V. Reva and T. N. Vorob'eva, Russ. J. Appl. Chem. **75**, 700 (2002).

38. F. Séby, M. Potin-Gautier, E. Giffaut, and O. F. X. Donard, Geochim. Cosmochim. Acta **65**, 3041 (2001).

39. Yu. Yu. Lur'e, *Handbook of Analytical Chemistry* (Khimiya, Moscow, 1989) [in Russian].

40. R. A. Yusupov and S. A. Bakhteev, Russ. J. Phys Chem. A **83**, 2188 (2009).

41. J. N. Butler, *Ionic Equilibrium: A Mathematical Approach* (Addison-Wesley, Reading, MA, 1964).

42. M. Pettine, F. J. Millero, and G. Macchi, Anal. Chem. **53**, 1039 (1981).

43. R. M. Cigala, F. Crea, and C. de Stefano, Geochim. Cosmochim. Acta **87**, 1 (2012).

44. T. Z. Din', R. A. Yusupov, and S. A. Bakhteev, Vestn. Kazan. Tekhnol. Univ. **15** (15), 49 (2012).

45. T. Z. Din', S. A. Bakhteev, and R. A. Yusupov, Vestn. Kazan. Tekhnol. Univ. **16** (17), 47 (2013).

46. T. Z. Din', S. A. Bakhteev, and R. A. Yusupov, Vestn. Kazan. Tekhnol. Univ. **16** (4), 92 (2013).

47. R. A. Yusupov, S. A. Bakhteev, and S. G. Smerdova, Russ. J. Phys. Chem. A **84**, 1263 (2010).

Translated by A. Muravev