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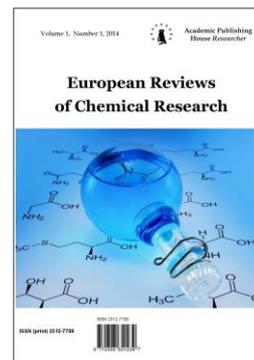
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Kinetic Aspects of Hydrochemical Deposition of Solid Phase Ag_2S

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Abstract

The article considers kinetic aspects study of hydrochemical deposition of solid phase Ag_2S from solutions containing silver nitrate, ammonium hydroxide and sodium citrate at temperatures 303-343 K in the conditions of the spontaneous formation of solid phase.

The authors conclude that:

1. Particular kinetic orders are defined on all components of reaction mixture and activation energy of this process is 37 kJ/mole.
2. In the certain concentration limits formal kinetic equation was derived for the rate of conversion of silver salt into silver sulfide that allows to provide the regulation of the rate of silver sulfide phase formation in the investigated reaction mixture purposefully.

Keywords: hydrochemical deposition, thiocarbamide, kinetic study, silver sulfide, formal kinetic equation, activation energy of chemical reaction.

1. Introduction

Growing interest to silver sulfide Ag_2S is associated with the possibilities of its use in functional electronics due to such properties as low band gap and high chemical stability in the form of nanostructural films, nanocrystals and quantum dots. Thin silver sulfide films are used in galvanic cells and photochemical cells [1, 2], photodetectors [3], solar energy converters [4, 5], sensor technology [6-10].

The practical use of such nanomaterials stimulates the search of possibilities of controlling their production processes. Today there is a great amount of data devoted to the production process of films and silver sulfide residues by both high temperature methods: thermal evaporation [2, 4, 11, 12], electro-deposition [5,13], molecular beam epitaxy (MBE) [14], gamma-irradiation [15], chemical deposition from vapour phase [16], sulfurization [17, 18], and low temperature methods: SILAR method [19, 20], chemical deposition [1, 21-23].

Despite the well-known opinion that it is more practical to use high temperature gas phase methods for the functional materials of optoelectronics, as they give minimum impurities, liquid phase methods have a number of advantages. First of all it is their technological simplicity and possibility of obtaining particles with controlled size.

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Among methods of liquid phase Ag_2S production we should emphasize the formation of nanoparticles by chemical deposition from aqueous medium. This is a well-behaved method for the synthesis of both separate sulfides CdS , ZnS , Cu_2Se , In_2S_3 , PbSe [24-29], and substitution solid solutions $\text{Cd}_x\text{Pb}_{1-x}\text{S}$, $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$, $\text{PbSe}_y\text{S}_{1-x}$, $\text{Cu}_x\text{Pb}_{1-x}\text{S}$, $\text{Cu}_2\text{S}-\text{In}_2\text{S}_3$ [30-34] for photodetectors, chemical sensors of toxic gases and heavy metals in aqueous media.

The analysis of publications on chemical deposition of films and powders of silver sulfide by thioamides indicates that there is still a question about mechanism of origin and growth of solid phase particles. To answer these questions it is important to do complex kinetic studies that allow to control and regulate the rate of the conversion of silver salt into sulfide purposefully.

Thus, this work is devoted to the kinetic study of deposition of Ag_2S phase by thiocarbamide in the citrate-ammoniac system and determination of the influence of each component content and temperature on the process rate.

2. Experimental

Kinetic study of chemical deposition of solid phase of silver sulfide Ag_2S by thiocarbamide was carried out in ammonia-citrated system in the conditions of spontaneous formation of solid phase with variations of component concentrations in the reaction mixture in the following ranges, mole/l: $[\text{AgNO}_3] = 3 \cdot 10^{-3} - 12 \cdot 10^{-3}$; $[\text{CS}(\text{NH}_2)_2] = 0.3 - 0.5$; $[\text{Na}_3\text{C}_6\text{H}_5\text{O}_7] = 0.1 - 0.3$; $[\text{NH}_4\text{OH}] = 0.5 - 4.0$. Deposition process was studied in the temperature range 303-343K with the accuracy of temperature control ± 0.1 degree. The necessity for temperature standardization and the sequence of reaction component decantation was caused by the fact that the rate of silver sulfide deposition process largely depends on the conditions of nucleation.

To determine the silver content in the solutions Volhard's method was applied with the use of 0.1M ammonium rhodanate solution over ferriammonium sulphates [35]. The titration was made until the appearance of persistent brownish-pink colour of the solution due to the interaction between SCN^- and Fe^{3+} ions. Analytical error was less 0.3%. Taking into account that thiocarbamide connects silver into stable molecular complexes before titration it was broken by sample boiling in concentrated nitric acid.

Excess concentration method suggested by Ostwald was used as a methodology of kinetic study and data interpretation [36, 37]. One of the parameters of the process was changed in each experiment (component concentration, temperature) at constant values of other parameters. Plotting of kinetic curves of deposition of Ag_2S phase was made by evaluation of residual silver in the reaction mixture in certain periods of time, until the equilibrium state in the system.

3. Results and discussion

Kinetic curves of silver salt conversion into sulfide have the typical form for heterogeneous autocatalytic processes which occur on the liquid – solid interface boundary (Fig.1). Figure 1 shows that the Ag_2S deposition process has a 5-minute induction period. Due to non-stoichiometric proportion of main components in the reaction system the equilibrium state appears at the time that is different from the time of the beginning of the process.

Particular order on silver salt was determined by graphical method comparing kinetic dependences in different coordinates [36]. It was estimated that in coordinates $\ln [\text{AgNO}_3] = f(\tau)$ experimental kinetic curves can be clearly described by the rate equation of the first order that demonstrates the first order of the process on silver salt (Fig. 1).

Kinetic curves of silver nitrate conversion in sulfide in the ammonia-citrated mixture depending on concentration changes of thiocarbamide, ammonium hydroxide, sodium nitrate are given in Fig. 2-4. From experimental data (Fig. 2), it is obvious that reaction between silver salt and thiocarbamide can't be described by whole-number values of stoichiometric coefficients. Particular order determined by the experiment on thiocarbamide $\text{CS}(\text{NH}_2)_2$ is minus 2.

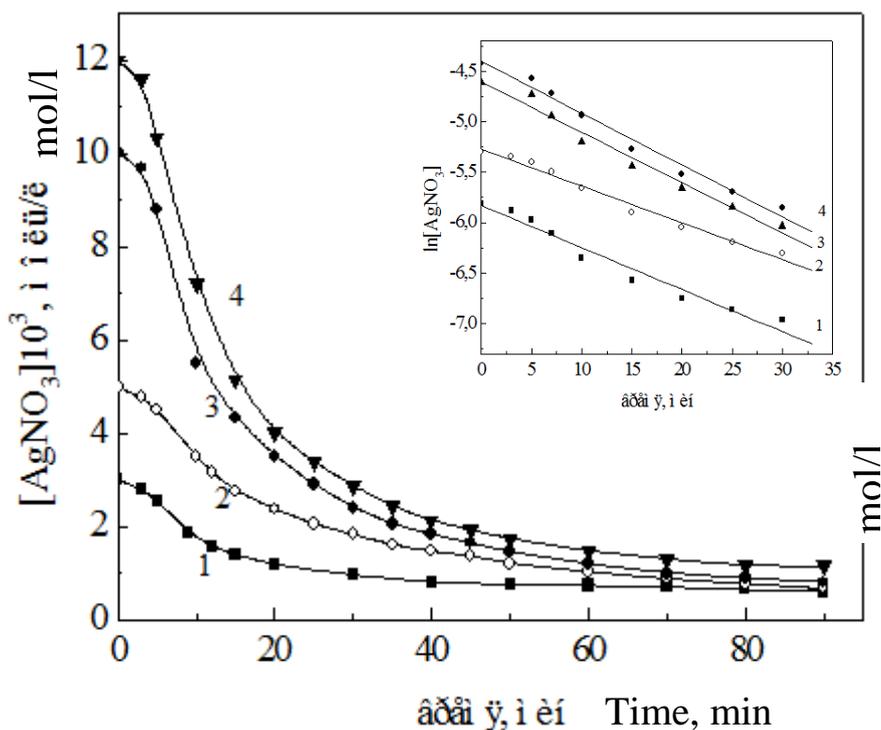


Fig. 1. Kinetic dependences of AgNO_3 conversion into sulfide at different initial metal salt concentrations in the reaction mixture, mole/l: 0.003, 0.005, 0.010, 0.012 and evaluation of particular order of the silver sulfide deposition by thiocarbamide on metal salt. Basic reaction mixture composition, mol/l: $[\text{Na}_3\text{C}_6\text{H}_5\text{O}_7] = 0.3$, $[\text{NH}_4\text{OH}] = 1.0$, $[\text{CS}(\text{NH}_2)_2] = 0.4$. Process temperature – 323 K.

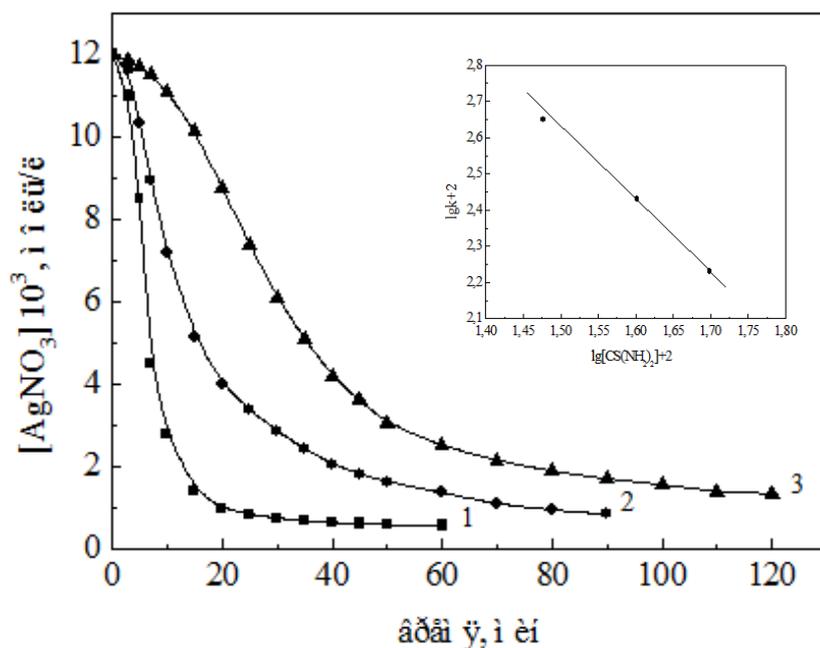


Fig. 2. Kinetic curves of Ag_2S deposition and evaluation of particular kinetic order of silver sulfide deposition on thiocarbamide at its different initial concentrations in reaction mixture, mole/l: 0.3 (1), 0.4 (2), 0.5 (3). Basic solution composition, mole/l: $[\text{AgNO}_3] = 0.012$, $[\text{Na}_3\text{C}_6\text{H}_5\text{O}_7] = 0.3$, $[\text{NH}_4\text{OH}] = 1.0$. Process temperature – 323 K.

The values of particular orders on sodium citrate and ammonium hydroxyl show that the concentration changes in the limits mentioned above doesn't influence on deposition process rate.

At the same time increasing of thiocarbamide content in the reaction mixture leads to significant slowing down of the reaction of silver sulfide formation. It is connected with the high value of instability constant of produced complex compound $\text{Ag}[\text{CS}(\text{NH}_2)_2]_3$ ($pK_{\text{H}} = 13.05$) in the system [38].

Fig. 5 shows that with the temperature increasing from 303 K to 343 K the range of the induction period gradually decreases to zero. The dependence of reaction rate constant versus temperature that is described by Arrhenius equation allows to calculate activation energy value and preexponential factor value. Evaluation of these parameters was made by graphic calculation of Arrhenius equation (Fig. 5). As a result activation energy of the Ag_2S formation (E_a) and preexponential factor in Arrhenius equation are 37.0 kJ/mole and $1.15 \cdot 10^4 \text{ s}^{-1} \cdot \text{mole}^{-0.7} \cdot \text{l}^{0.7}$ correspondingly. The obtained value of activation energy shows that the deposition process predominantly occurs in the kinetic range.

Taking into account the obtained values of particular kinetic orders on reactants and activation energy, formal kinetic equation of conversion rate of silver salt into Ag_2S in the conditions of spontaneous formation of solid phase in citrate-ammoniac system at different reactant contents in the concentration limits mentioned above can be expressed as:

$$W_{\text{Ag}_2\text{S}} = 1.15 \cdot 10^4 \cdot \exp\left(-\frac{37.0 \cdot 10^3}{8.31 \cdot T}\right) \cdot S \cdot C_{\text{Na}_3\text{C}_6\text{H}_5\text{O}_7}^{0.3} \cdot C_{\text{NH}_4\text{OH}}^{-0.2} \cdot C_{\text{CS}(\text{NH}_2)_2}^{-2.0} \cdot C_{\text{AgNO}_3},$$

where S is the area of the produces solid phase.

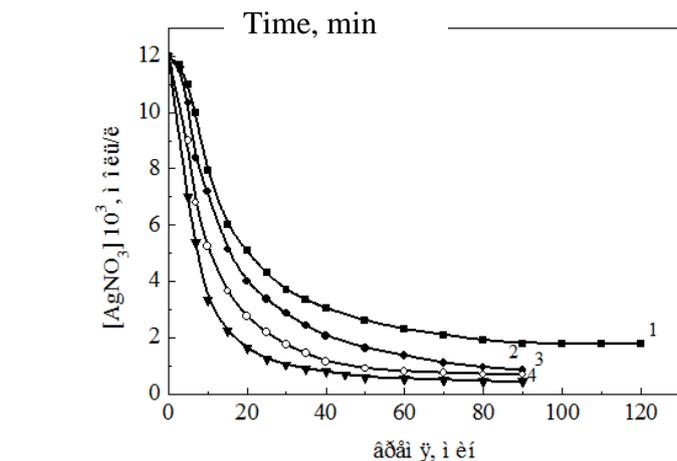
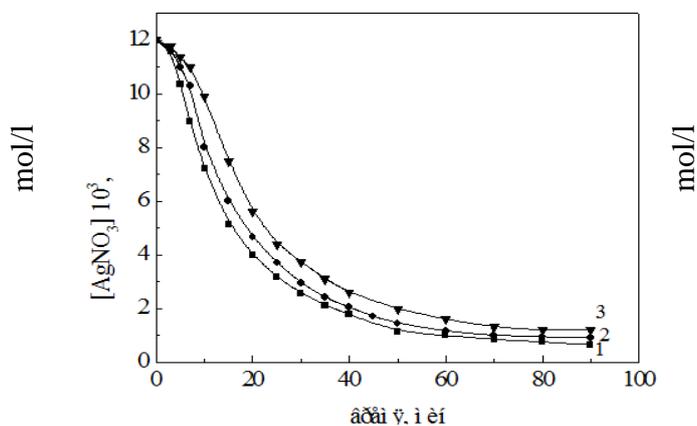


Fig. 3. Kinetic curves of Ag_2S deposition at different initial sodium nitrate concentration $[\text{Na}_3\text{C}_6\text{H}_5\text{O}_7]$ in the reaction mixture, mole/l – 0.3 (1), 0.2 (2), 0.1 (3). The solution composition, mole/l: $[\text{AgNO}_3] = 0.012$, $[\text{NH}_4\text{OH}] = 1.0$, $[\text{CS}(\text{NH}_2)_2] = 0.4$. Process temperature: 323K.

Fig. 4. Kinetic curves of Ag_2S deposition at different initial ammonium hydroxyl $[\text{NH}_4\text{OH}]$ in the reaction mixture, mole/l – 0.5 (1), 1.0 (2), 2.0 (3), 4.0 (4). The solution composition, mole/l: $[\text{AgNO}_3] = 0.012$, $[\text{Na}_3\text{C}_6\text{H}_5\text{O}_7] = 0.3$, $[\text{CS}(\text{NH}_2)_2] = 0.4$. Process temperature – 323 K.

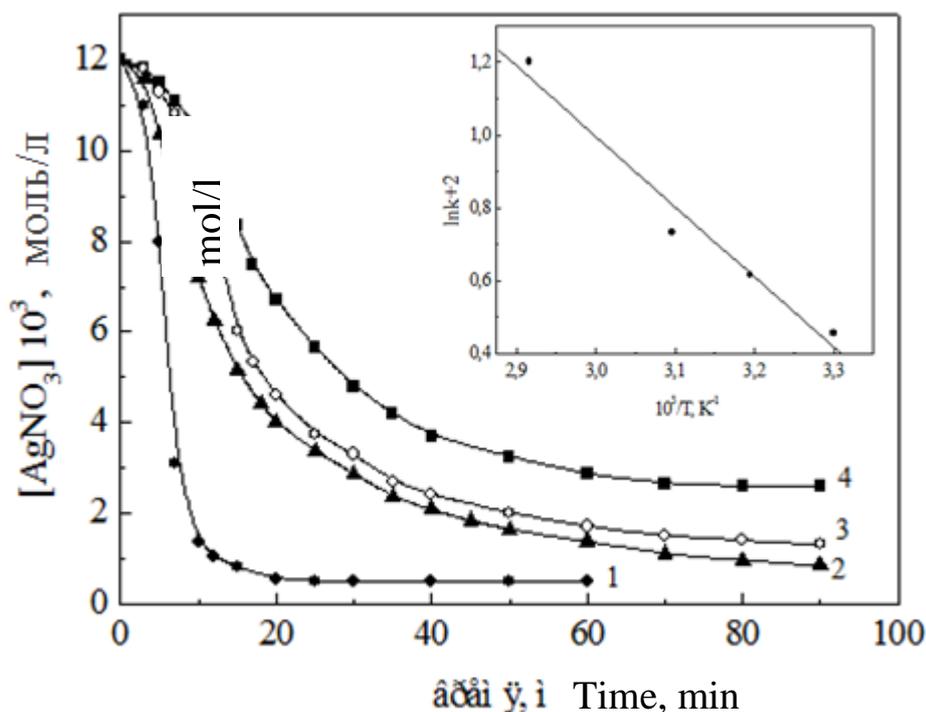


Fig. 5. Kinetic curves of Ag_2S deposition (a) at different process temperature, K: 343 (1), 323 (2), 313 (3), 303 (4) and activation energy evaluation (b). Reaction mixture composition, mole/l: $[AgNO_3] = 0.012$, $[Na_3C_6H_5O_7] = 0.3$, $[NH_4OH] = 1.0$, $[CS(NH_2)_2] = 0.4$.

Derived formal kinetic equation clearly shows the contribution of each component of the reaction mixture and temperature to the process rate. Thus, on the one hand, increasing of ammonium concentration and particularly thiocarbamide inhibits Ag_2S formation, on the other hand, sodium nitrate influence on the rate is conversed. Probably, it is the result of its intense buffered action, considering that $Na_3C_6H_5O_7$ is a weak tribasic acid salt.

Kinetic equation allows to change the rate of silver sulfide deposition purposefully by varying the component content in the reaction mixture and temperature values. It is an effective instrument for both intensity regulation of nucleation process and particle size of the produced solid phase. Its practical use provides the quick formation of required compound composition of the reaction mixture and allows to decrease the number of searching experiments.

4. Conclusion

1. The complex kinetic study of hydrochemical deposition of silver sulfide in the conditions of spontaneous nucleation of solid phase in the system containing silver nitrate, thiocarbamide, ammonium hydroxide and sodium citrate was made for the first time. The first particular order on silver salt was estimated experimentally. Particular kinetic orders on thiocarbamide, ammonium hydroxide and sodium nitrate were determined: -2.0, -0.2 and 0.3 correspondingly. Activation energy of the process calculated using Arrhenius equation is 37.0 kJ/mole.

2. Formal kinetic equation of the conversion rate of silver salt into Ag_2S in the conditions of spontaneous nucleation of solid phase was introduced. Its use in a certain concentration limits allows to vary nucleation rate and particle size of the deposited silver sulfide purposefully.

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