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Kinetics of Formation of Potassium Hydroxyaluminosilicate in Aqueous KOH Solution

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Abstract—The time in which a supersaturated aqueous-alkaline aluminosilicate solution is stable to phase transformation was studied in relation to the solution composition and temperature. Empirical equations were suggested describing how the induction period of potassium hydroxyaluminosilicate formation depends on the solution composition, temperature, and supersaturation factor. These equations allow prediction of the compositions of stable solutions and evaluation of the enthalpy (25.6 kJ mol^{-1}) and entropy (126.2 J mol^{-1} K^{-1}) of solution, the activation energy (19.1 kJ mol^{-1}) of formation of potassium hydroxyaluminosilicate $KAlSiO(OH)_6$, and the induction period of formation of the solid phase.

Procedures for production of modern materials often involve formation of inorganic and organometallic compounds in aqueous and nonaqueous solutions [1, 2]. Fluctuation processes permanently occurring in solutions involve reversible formation and breakdown of various associates [3]. In labile (unstable) supersaturated solutions, the forward chemical reaction of compound formation prevails, whereas in unsaturated solutions the prevailing process is dissolution. The rate ratio of compound formation and dissolution depends on the solution composition and temperature. In metastable supersaturated solutions, a labile equilibrium, also governed by the solution composition and temperature, can occur for a certain time. Labile and metastable supersaturated solutions differ in the time of the initial stage of the phase transformation (induction period). As the concentration of reactants in the initial solution is increased, or the solubility of the product is decreased, colloidal precipitates are formed [4]. The induction period of formation of crystalline precipitates as a function of the solution composition is described by classical linear equations based on the law of mass action or on the supersaturation factor [5, 6]. For the kinetics of sol formation in solutions, these equations are nonlinear [7, 8].

In this work, we studied the kinetics of the initial stage of the solid phase formation as influenced by the solution composition, temperature, and supersaturation factor.

Formation or dissolution of potassium hydroxyaluminosilicate in aqueous KOH solution can be described by the following equation:

$$K_m[SiO_m(OH)_{4-m}] + (m - 1)H_2O + K[Al(OH)_4] \rightleftarrows K[AlSiO_4]\cdot 2H_2O\downarrow + H_2O + mKOH, \quad m = 1\text{–}2. \qquad (1)$$

The rate of the forward reaction in the initial stage of potassium hydroxyaluminosilicate in solution is

$$V = k_1(\mathrm{CP})^{n-1}, \qquad (2)$$

where k_1 is the rate constant, CP is the concentration product of potassium aluminate and silicate in supersaturated solution, and n is the number of potassium hydroxyaluminosilicate formula units in the forming particles.

The initial stage of reaction (1) lasts until a certain critical concentration of potassium hydroxyaluminosilicate particles C_{PHAS} is attained (this takes time t_{i}), after which the particles undergo rapid aggregation to reach a size at which light scattering is observed [7]. Correspondingly,

$$t_i = C_{\mathrm{PHAS}}/V = k_2(\mathrm{CP})^{1-n}. \qquad (3)$$

The equilibrium constant K_e of heterogeneous reaction (1) in solution is defined as the ratio of the concentration product CP_e of potassium aluminate and silicate to the KOH concentration C_{KOH} raised to power m.

$$K_e = \mathrm{CP}_e/C^m_{\mathrm{KOH}}. \qquad (4)$$

Here, $\mathrm{CP}_e = C_{K[Al(OH)_4]}C_{K_m[SiO_m(OH)_{4-m}]}$ is the value corresponding to the equilibrium with the potassium hydroxyaluminosilicate precipitate.

Table 1. Induction periods t_i (s) of sol formation at 20°C, molar ratio $SiO_2/KAlO_2$ = 1, and different values of CP (cmol^2 l^{-2}) and alkali concentration. Calculated coefficients a_1 and b_1 of Eq. (6)

Parameter	Value					
	10.2 M KOH					
CP	1225	900	625	400	–	–
t_i	6	8	14	58	–	–
a_1	9.95 ± 0.80					
b_1	–4.79 ± 0.42					
	5.1 M KOH					
CP	351.56	306.25	225	189	156.2	–
t_i	8	9.5	19.5	36	58	–
a_1	9.02 ± 0.34					
b_1	–4.69 ± 0.20					
	2.55 M KOH					
CP	156.25	126.5	112.9	100	87.9	76.56
t_i	9.5	14	17.5	24	29	43
a_1	6.22 ± 0.20					
b_1	–3.33 ± 0.13					
	1.275 M KOH					
CP	39.0	36.58	34.33	32.28	30.41	28.69
t_i	43	49	57	64	76	84
a_1	3.80 ± 0.07					
b_1	–1.90 ± 0.05					
	0.85 M KOH					
CP	156.25	100	69.44	54.42	44.44	34.02
t_i	7.9	10.5	14.4	18.4	22	30
a_1	2.99 ± 0.04					
b_1	–1.40 ± 0.03					

The experimental data on the induction periods t_i of sol formation in solutions of different compositions at a constant temperature are given in Table 1. These data can be described (in a narrow range of variation of the initial solution composition, at constant alkali concentration and molar ratio $SiO_2/KAlO_2 \approx 1$) by the logarithmic form of Eq. (3):

$$\ln t_i = a + b\ln \mathrm{CP}. \qquad (5)$$

The average number n of potassium hydroxyaluminosilicate formula units in particles formed during the induction period is $1 - b$.

In the whole range of the solution compositions studied, the experimental data are not fitted by linear equation (5). The kinetic equation can be linearized by taking logarithms of some variables once more:

$$\ln\ln t_i = a_1 + b_1\ln\ln \mathrm{CP}, \qquad (6)$$

$$\ln\ln t_i = a_2 + b_2\ln \mathrm{CP}, \qquad (7)$$

$$\ln t_i = a_3 + b_3\ln\ln \mathrm{CP}. \qquad (8)$$

From data in Table 1, we calculated the coefficients of Eqs. (5)–(8) for the corresponding alkali concentrations in solution. Then, by Eqs. (5)–(8), we calculated the concentration products for solutions with the preset time of stability to sol formation of 100 h ($\mathrm{CP_e}$). The calculated $\mathrm{CP_e}$ values are plotted in Fig. 1. The compositions calculated by Eq. (6) coincide with the results of the chemical analysis of the liquid phases of the gels (Table 2). The CP values calculated by Eq. (7) only roughly approximate the results of analysis of the liquid phases, being fully inconsistent for weakly alkaline solutions. The equilibrium com-

Table 2. Compositions of potassium aluminosilicate aqueous sols and their liquid phases at 20°C; calculated compositions of solutions stable to sol formation for 100 h at 20°C and molar ratio MR = $SiO_2/KAlO_2$ = 1; and coefficients $\ln K_e$ and *m* of Eq. (9) for the corresponding solutions

Sol composition, M			Liquid phase composition, M					Calculated solution compositions	
KOH	$KAlO_2$	SiO_2	KOH	$KAlO_2$, $\times 10^2$	SiO_2, $\times 10^2$	MR	$CP \times 10^4$	KOH	$CP \times 10^4$
0.85	0.125	0.125	0.732	2.56	1.11	0.43	2.84	10.2	108.7
3.4	0.500	0.50	2.88	9.14	3.13	0.34	28.6	5.1	53.19
3.4	0.400	0.60	2.86	2.12	12.5	5.89	26.5	2.55	20.11
5.1	0.333	0.333	4.66	6.52	5.66	0.87	36.9	1.275	6.87
5.1	0.250	0.250	4.60	7.40	6.00	0.81	44.4	0.85	3.92
			$\ln K_e$ −7.61±0.16, *m* 1.46±0.14					$\ln K_e$ −7.53±0.07, *m* 1.34±0.05	

positions of solutions predicted by Eq. (8) and especially by Eq. (5) strongly differ from the analytical results for the liquid phases in the entire range of the alkali concentrations. The concentrations of aluminate and silicate components in the liquid phases of the gels and their calculated concentrations in quasiequilibrium solutions increase with increasing alkali content (Fig. 1). The calculated and experimental concentrations of the aluminate and silicate components were compared for the equivalent alkali content and constant temperature, using the logarithmic form of Eq. (4):

$$\ln CP_e = \ln K_e + m \ln C_{KOH}. \qquad (9)$$

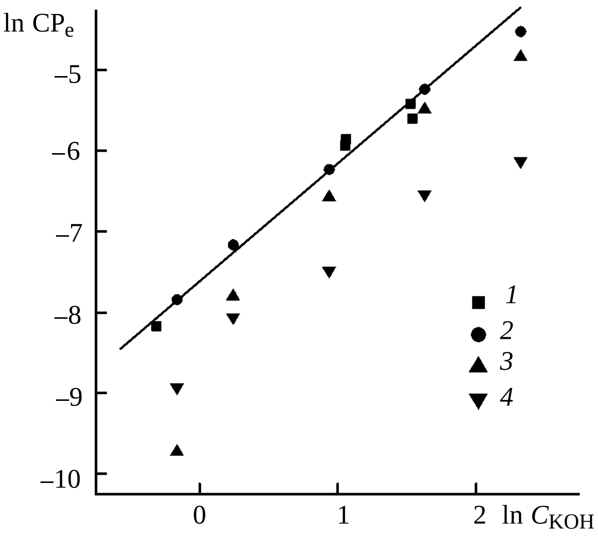

Fig. 1. Concentration product CP_e of aluminate and silicate as a function of KOH concentration C_{KOH} in solutions with the molar ratio $SiO_2/KAlO_2 \approx 1$ at 20°C: (*1*) in analyzed liquid phases of gels and (*2*–*4*) in solutions stable to sol formation for 100 h as calculated by Eqs. (6)–(8), respectively.

The equilibrium constants K_e and coefficients m of Eq. (9) coincide within determination error (Table 2) both for the calculated compositions of solutions stable to sol formation and for the compositions of the liquid phases of the sols. The calculated CP_e values and those determined by analysis, at equivalent alkali concentrations, also coincide within the error (Fig. 1). It should be noted that, in Eq. (6), to make possible taking the logarithm twice, the component concentrations are expressed in cM, and in Eq. (9), in M.

The CP values calculated by Eq. (6) for the induction periods ranging from 10 to 100 h vary only slightly and are close to the CP values for solutions stable to sol formation and to the values obtained by analysis of liquid phases of aqueous potassium aluminosilicate sols.

It is of particular interest to predict, on the basis of experimental data on stability of solutions to sol formation, the temperature dependence of the compositions of the sol–gel liquid phases. The temperature dependence of the reaction rates in solutions of constant composition is described by the Arrhenius equation reflecting an increase with temperature in the relative content of components capable of overcoming the energy barrier. Table 3 shows that, for the experimental solution of a constant composition (CP 625 $cmol^2\ l^{-2}$, 10.2 M KOH), the induction period of the sol formation decreases from 14 to 7 s as the temperature is increased from 20 to 40°C; however, as the temperature is increased further, from 40 to 70°C, the induction period starts to increase, reaching 300 s. For the given constant composition of the aqueous potassium aluminosilicate solution, the kinetics of the sol formation cannot be described by the Arrhenius

Table 3. Influence of temperature and solution composition on the induction period t_i (s) of sol formation[a] and on the coefficients a_1 and b_1

CP	t_i						
	20°C	30°C	40°C	50°C	60°C	70°C	80°C
1225	6						4
1139							6.5
1056						4	11
976							23
900	8	5				12.5	42
756				6.5	9	24	
689					16	90	
625	14	9	7.5	14	38	300	
506		19	18	40			
400	58	39	60				
	Coefficient values						
a_1	9.9±0.8	13.1±0.7	19.0±0.9	21.1±0.9	34.9±1.6	33.8±3.0	44.4±2.8
b_1	–4.8±0.4	–6.6±0.4	–9.8±0.5	–10.8±0.5	–18.0±0.8	–17.2±1.6	–22.4±1.4

[a] The solution contains 10.2 M KOH; molar ratio $SiO_2/KAlO_2$ = 1. The concentration product CP of silicate and aluminate in solution is expressed in $cmol^2 l^{-2}$.

equation, probably, because of the appreciable temperature dependence of the solubility of the sol solid phase. With increasing temperature, a supersaturated solution can become saturated and unsaturated.

The supersaturation factor S in aqueous aluminosilicate solution (at the molar ratio $SiO_2/KAlO_2$ = 1 and constant alkali content) was determined as the ratio of the concentration product PC of the aluminate and silicate components to the solubility product CP_e of the solid phase under similar conditions. The solubility product can be determined by analysis of the liquid phases of the sols or calculated from kinetic data and Eq. (6) for the corresponding temperatures. From data in Table 3, using Eq. (6), we calculated the CP values for solutions stable to sol formation for 100 h (CP_e) at different temperatures. The calculated solubility of amorphous aluminosilicate in aqueous KOH noticeably increases with temperature, obeying the Arrhenius equation:

$$\ln CP_e = A_0 + B_0/T, \qquad (10)$$

where $B_0 = (-3085 \pm 119) = \Delta H/R$, ΔH is the enthalpy of solution, $R = 8.31441$ J mol^{-1} K^{-1} is the universal gas constant, A_0 $(15.2 \pm 0.4) = \Delta S/R$, where ΔS is the entropy of solution.

Using Eq. (10), we calculated the enthalpy (25 kJ mol^{-1}) and entropy (126 J mol^{-1} K^{-1}) of solution of amorphous aluminosilicate in aqueous KOH. From the calculated CP_e values and data in Table 3, we calculated the supersaturation factors $S = CP/CP_e$ for different temperatures and the measured induction periods of sol formation, at a constant content of the alkali. These data obey Eq. (11) in a wide range of compositions of experimental solutions (Fig. 2):

$$\ln\ln t_i = \ln\ln t_0 + \eta \ln S. \qquad (11)$$

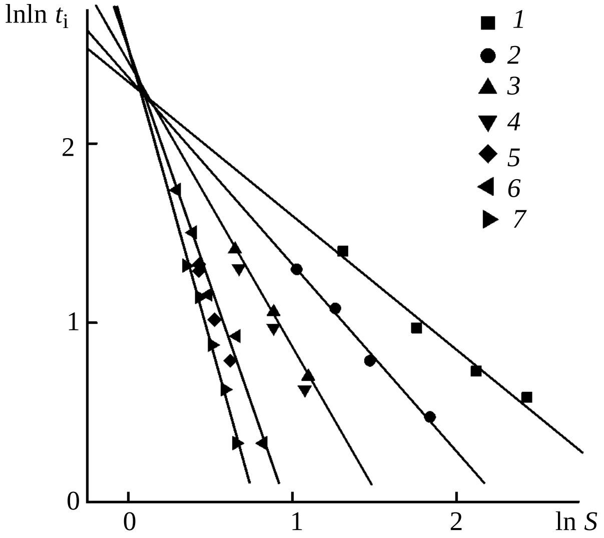

Fig. 2. Induction period t_i of sol formation as a function of the supersaturation factor in aqueous-alkaline (10.2 M KOH) aluminosilicate solution. Temperature, °C: (*1*) 20, (*2*) 30, (*3*) 40, (*4*) 50, (*5*) 60, (*6*) 70, and (*7*) 80.

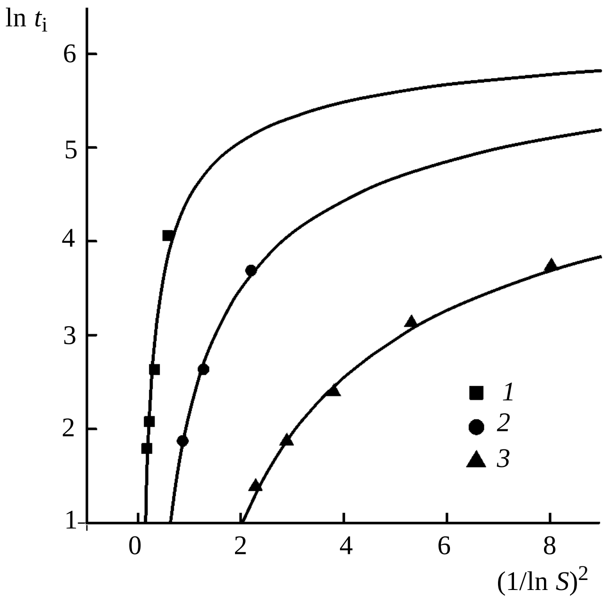

Fig. 3. Induction period t_i of sol formation in aqueous-alkaline (10.2 M KOH) aluminosilicate solution as a function of the supersaturation factor S. Temperature, °C: (*1*) 20, (*2*) 50, and (*3*) 80. The curves correspond to experimental dependence (14) plotted in coordinates of Eq. (15).

The numerical value of $\ln\ln t_0$ is approximately equal for different temperatures, ranging from 2.35 (20°C) to 2.50 (80°C), with the mean value being 2.4 ± 0.2.

The expected time t_0 in which the concentration of aluminosilicate particles in the saturated solution attains a critical level reflects the rate of forward reaction (1) of formation of aluminosilicate particles in the liquid phase in equilibrium with the sol solid phase. Under these conditions, the rates of the forward and reverse reactions are equal. Attainment of the critical concentration of aluminosilicate particles for sol formation is hardly probable, and nuclei of the solid phase of the critical size can be formed by a "homogeneous" mechanism [3] only for a short time as a result of fluctuations.

The slope of linear equation (9) varies with temperature (Fig. 2). The coefficient η (a function of the number of potassium hydroxyaluminosilicate formula units in the critical nucleus) depends on temperature:

$$\ln(-\eta) = \ln\gamma + B/T \qquad (12)$$

with $\ln\gamma = 8.5\pm0.8$ and $B = -2547\pm253$.

The induction period of sol formation in solution depends on the supersaturation factor and on the solution temperature as follows (for 10.2 M KOH):

$$\ln t_i = (\ln t_0)S^{-\gamma\exp B/T}. \qquad (13)$$

This equation reflects the kinetics of the forward reaction of formation of aluminosilicate particles: In supersaturated ($S > 1$) solutions, raising temperature accelerates forward reaction (1) of formation of aluminosilicate particles, and in unsaturated ($S < 1$) solutions, decelerates this reaction.

In a narrow range of supersaturation factors, the experimental data can be fitted by Eq. (14) [9] with the following coefficients: for 20°C, $a = 6.5\pm0.7$, $\beta = -2.0\pm0.4$; for 50°C, $a = 6.7\pm0.2$, $\beta = -4.5\pm0.3$; and for 80°C, $a = 6.4\pm0.1$, β -7.7 ± 0.3.

$$\ln\ln t_i = a + \beta\ln S. \qquad (14)$$

The number of formula units in the critical particle in the induction period of sol formation can be estimated on the basis of the law of mass action as $n = 1 - \beta$. In particular, as the temperature is increased from 20 to 80°C, n increases from 3 to 9.

The classical kinetic equation for formation of nuclei of a new phase has the form

$$\ln t_i = F + D/(\ln S)^2, \qquad (15)$$

where F is a certain coefficient and $D = (16\pi\sigma^3v^2)/3\times(kT)^{-3}$ (σ is the specific surface energy, v is the molecular volume, k is the Boltzmann constant, and T is the temperature).

Experimental data and the curves corresponding to Eq. (14) in the coordinates of Eq. (15) are plotted in Fig. 3 for different temperatures. At a constant temperature, the coefficient B (slope of the curve) varies depending on the supersaturation factor, i.e., the number of potassium hydroxyaluminosilicate formula units in the critical nucleus increases with decreasing supersaturation factor.

Figure 4 shows how the induction period of sol formation depends on the supersaturation factor at different concentrations of alkali in solution and constant temperature. For the KOH concentration range 2.5–10.2 M and 20°C, the effect of supersaturation on the induction period of sol formation is described by Eq. (11) with the coefficients equal within the determination error. In other words, in this range of KOH concentrations the kinetics of sol formation depends on the supersaturation factor and temperature. As the KOH concentration in solution is decreased from 2.5 to 0.85 M, the slope of Eq. (11) (coefficient η) changes.

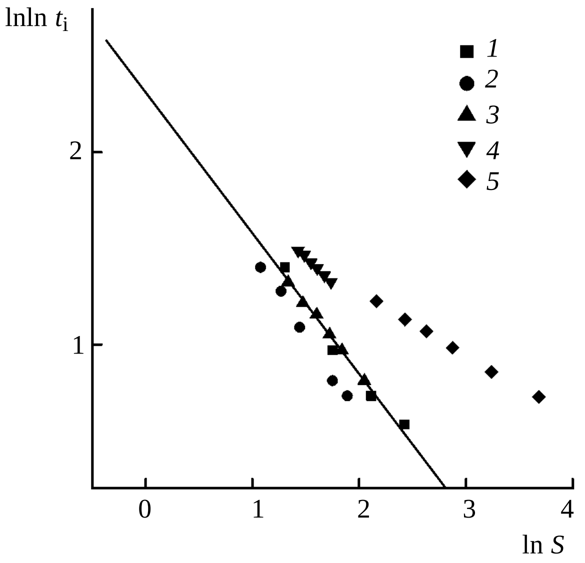

Fig. 4. Induction period t_i of sol formation at 20°C as a function of the solution supersaturation factor *S*. KOH concentration, M: (*1*) 10.2, (*2*) 5.1, (*3*) 2.55, (*4*) 1.275, and (*5*) 0.85.

EXPERIMENTAL

To prepare the initial silicate solution, a 60-g portion of ultrapure grade silica (moisture content 2.4 wt %, as determined from the weight loss upon calcination at 1000°C) was dissolved on heating in 673.2 g of granulated KOH (analytically pure grade). The resulting transparent solution was cooled and diluted with distilled water to a volume of 1 l in a volumetric flask. To prepare the initial aluminate solution, 27.0 g of spectroscopically pure aluminum turnings was dissolved in 673.2 g of granulated KOH (analytically pure grade). The resulting transparent solution was cooled and diluted with distilled water to a volume of 1 l. The initial KOH solution was prepared by dissolving 673.2 g of granulated KOH (analytically pure grade, moisture content 15 wt %) in distilled water; the resulting solution was cooled to 20°C and brought to a volume of 1 l. The alkali content in solution, estimated from the solution density at 20°C, was 10.2 M; the same value was obtained by common acid–base titration.

Supersaturated solutions of potassium hydroxyaluminosilicates were prepared by mixing equal volumes of the aqueous-alkaline aluminate and silicate solutions with an equivalent KOH content. The initial aqueous KOH solution (5–20 ml) was mixed with 10–20 ml of the initial potassium aluminate solution, and, after 10–15 min, the mixture was quickly added to 10–20 ml of a stirred (60 rpm) potassium silicate solution. The solutions were preliminarily kept for 1 h at the chosen temperatures and mixed in temperature-controlled cells. Solutions with a lower KOH concentration were prepared by diluting the initial solutions with distilled water.

As the induction period t_i of sol formation in solution, we took the time from the start of mixing of the silicate and aluminate solutions in the cell to the moment when the intensity of light scattering in the cell (at side illumination against a dark background) increased [7]. The maximal deviations of the results of ten measurements from the mean value did not exceed 5%. In most cases, the induction periods varied within 10–60 s.

Hermetically sealed fluoroplastic test tubes with the resulting sols (molar ratio $SiO_2/KAlO_2 \approx 1$) were kept at a chosen temperature for 1 h and then centrifuged for 10 min at 5000–6000 rpm. The liquid phases of the squeezed sols were separated, diluted, and analyzed (for K with a flame photometer, for Al by titration, and for Si colorimetrically [9]).

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