

Пропонується універсальна розрахункова модель для теоретичного опису структурних і фізико-хімічних властивостей водних розчинів модифікованих силікатів за участю комплексотворювачів. Модель враховує три типи рівноваг: кислотно-основні, метало-комплексні і, для кремнекисневих аніонів (ККА), також поліконденсаційні. Розроблений математичний апарат допускає застосування моделі практично до будь-яких типів рідких стекел та їх сумішей. Для окремого випадку натрій-цинк-амонійного рідкого скла модель передбачає чисельне рішення системи з сімнадцяти лінійних і нелінійних рівнянь методом Ньютона.

Нова модель була використана для пояснення спостережуваного експериментально ефекту реологічної аномалії в водних розчинах рідкого скла, модифікованого цинком і аміаком. Ефект характерний, більш за все, для розчинів аminosилікатів, де реологічна аномалія пов'язана зі зміщенням при нагріванні молекулярно-масового розподілу (ММР) ККА в напрямку процесу поліконденсації. Результати розрахунків показують, що подібне зміщення має місце також в даній системі і пояснюється трансформацією амінокомплексів цинку в гідроксокомплекси. Сумарний процес може бути виражений рівнянням $[Zn(NH_3)_4]^{2+} + 3OH^- \rightarrow [Zn(OH)_3]^- + 4NH_3$, що пояснюється істотною відмінністю величин ентальпії утворення цих комплексів. Це призводить до зменшення величини рН і до зміщення ММР ККА в сторону підвищення ступеня полімеризації (зменшення середньої основності ККА). Присутність інших комплексних частинок, таких як $[Zn(NH_3)_3]^{2+}$, $[Zn(OH)_4]^{2-}$, $[Zn(OH)_2]$ і т. д., не відіграє суттєвої ролі.

Використання запропонованої моделі дозволило розрахувати залежності параметрів ММР ККА, величин рН і концентрацій комплексних і поліконденсаційних структур від складу розчину і температури. Детально простежено еволюцію відносного змісту різних структур, що містять цинк і кремній, в ході зміни температури і загальної концентрації цинку. Зроблено висновок про те, що реологічна аномалія в досліджуваній системі існує завдяки особливому поєднанню термодинамічних параметрів і навряд чи широко поширена серед метало-комплексних силікатів

Ключові слова: розчинні силікати, модифіковані рідкі скла, комплекси цинку, аномальна реологія, поліконденсація

MODELING A RHEOLOGICAL ANOMALY IN THE SYSTEM $Na_2O-SiO_2-NH_3-ZnO-H_2O$

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1. Introduction

Aqueous solutions of silicates are widely used in industry and construction (glues, protective coatings, acid-resistant concretes, insulation materials and much more). Currently, four types of water-soluble silicates (WSS) are known: alkaline silicates (AS), tetrasubstituted ammonium silicates (TAS), amino silicates (AMS) and metal-complex silicates (MCS). Aqueous solutions of WSS of the latter three types are sometimes called alkaline-free liquid glasses. Mixed liquid glasses, for example, based on AS and AMS [1], AS and MCS [2] are also known.

In aqueous solutions of silicates, there can be five types of ion-molecular equilibria with appropriate equilibrium constants, in turn, depending on temperature. These are water dissociation, dissociation of silanol groups and polycondensation of silicate oxygen anions SOA (all types of WSS), as well as the protonization of amino groups (AS and MCS) and dissociation of complex ions (MCS). These equilibrium constants determine the most important structural and chemical characteristics of solutions: parameters of molecular mass distribution (MMD) of SOA, pH value and many others.

A very important structural-sensitive property of solutions of some WSS is the rheological anomaly, expressed in

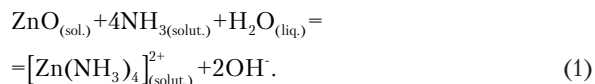
the reversible increase in viscosity when heated, up to gelation. This effect was found in the solutions of most AS silicates [3], as well as in solutions of lithium silicates [1], and in sodium-zinc-ammonia liquid glass (ZAWG) [4]. It was found that, at least in AS solutions, the anomaly is accompanied by a noticeable increase in polycondensation of SOA at heating.

At the same time, the existence of a rheological anomaly in aqueous solutions of silicates with cations – residues of strong bases (lithium and tetramminzinc), has not been explained yet. Without thermodynamic modeling of the rheological anomaly in these systems, it is impossible to create the fundamentals of the general theory of rheological anomaly in water-silicate systems. The problem of designing some common criteria for the search of new water-silicate and other inorganic systems with a rheological anomaly remains equally important. This is also essential from the practical point of view, given their possible applications in various technologies.

2. Literature review and problem statement

The method for obtaining ZAWG from sodium liquid glass, aqueous solution of ammonia and solid zinc oxide was

first described in paper [4]. A homogeneous solution, stable when stored in the absence of ammonia evaporation, is formed on conditions that $[\text{SiO}_2]/[\text{ZnO}] \geq 10$ and $[\text{NH}_3]/[\text{ZnO}] \geq 4.2$. The chemical reaction that occurs at the same time can be conventionally recorded as follows:



The existence of a rheological anomaly in the resulting system was reported in research [7]. As an example, Fig. 1 shows the temperature dependences of the decimal logarithm of dynamic viscosity (η , mPa·s.) of sodium water glass with molar module 2.9, its mixture with 12 % by weight of 28 % water solution of ammonia and ZAWG, obtained by dissolution of 4 % by weight of zinc oxide in this mixture.

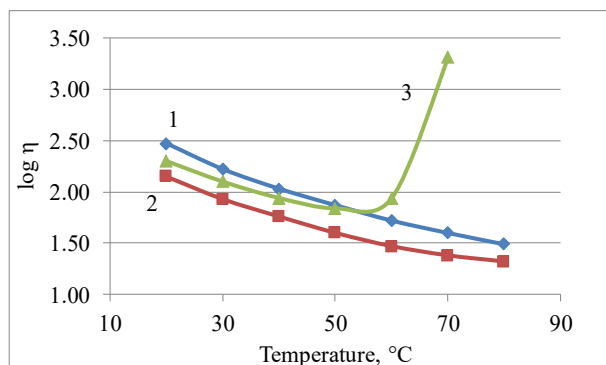


Fig. 1. Temperature dependence of the logarithm of dynamic viscosity (η) according to the data [7]: 1 – solution $\text{Na}_2\text{O} \cdot 2.9\text{SiO}_2$, 2 – solution $\text{Na}_2\text{O} \cdot 2.9\text{SiO}_2 + \text{NH}_3$, 3 – ZAWG

According to the experimental data [1, 8], there is no rheological anomaly in solutions of strong-base silicates (except lithium silicates). Accordingly, curves 1 and 2 show a monotonous decrease in viscosity with temperature. In contrast, curve 3 shows the presence of a rheological anomaly at temperatures above 55 °C. This behavior is observed for any sufficiently concentrated ZAWG having a molar silicate module above two.

Reliable explanations of the cause of existence of the rheological anomaly in this system are still missing. It has been suggested that it is a significant endothermicity of the reaction of decomposition of amino complex of zinc, which leads to the disintegration of the complex with the formation of insoluble zinc hydroxide [8]. However, this explanation is contradicted by the fact that solutions of silicates of other complex cations with similar thermodynamics, for example, of ammonia of copper and nickel, do not show a rheological anomaly. The decisive role of an ammonium cation as a weak-base ion in the anomaly occurrence by the AS mechanism is extremely unlikely, as evidenced by the results of mathematical modeling for the system $\text{NH}_3\text{--SiO}_2\text{--H}_2\text{O}$ [5]. In non-zinc mixtures “water glass + ammonia” under some conditions there is the gel formation at heating [7], but the resulting gels are non-reversible.

The external features of the rheological anomaly in all silicate solutions, where it occurs, are very close. This is, for example, the quasi-homogeneity of the gel, its non-smelting at further heating, the width of viscosity hysteresis in the cycles “heating – cooling” of about 10 minutes. This is very likely to indicate a unified mechanism for the occurrence of

an anomaly in such systems and the possibility of its theoretical description within a single mathematical model.

In article [6], the mathematical model of the silicate aqueous solution, based on the following assumptions, was proposed and subsequently improved [8]:

- aqueous solutions of WSS are of the thermodynamical equilibrium nature;
- the magnitude of dynamic viscosity of silicate solutions is directly related to the average degree of polymerization of SOA;
- the magnitude of the constant of dissociation of the silanol groups of SOA and equilibrium constants of the SOA polycondensation process do not depend on the structure of anion and its degree of polymerization, as well as on the type of cation.

The first two assumptions are based on the totality of the results of research into aqueous solutions of WSS [1], and the third one is a quite acceptable simplification that makes the calculation much easier and partially relies on the results of experimental studies [9, 10]. Molar concentrations of silica and cation, as well as the magnitudes of constants of dissociation and polycondensation of silanol groups, were used as source data. At the output, we obtained the concentrations of various structural elements of SOA ($\equiv\text{Si}\text{--OH}$, $\equiv\text{Si}\text{--O}^-$ and $\equiv\text{Si}\text{--O}\text{--Si}\equiv$), the average basicity of SOA and a pH value.

The latest version of the calculation model [8] allowed explaining several non-trivial experimentally observable effects. They include the existence of a rheological anomaly in AMS solutions, its absence in the solutions of AS and TAS, as well as the monomeric nature of silicic acid in the solution. However, this model cannot be applied to MCS solutions, and therefore, to ZAWG, as it does not take into consideration the equilibria of decomposition of complex ions.

However, with some complication, this calculation model can be used as the basis for creating a universal model suitable for describing the properties of all types of WSS solutions, including for explaining the existence of the rheological anomaly in ZAWG. An important condition for this is the existence of a set of reliable thermodynamic parameters of complex ions, in particular, numerous zinc-containing cations and anions, the formation of which is possible in the system $\text{Na}_2\text{O}\text{--SiO}_2\text{--NH}_3\text{--ZnO}\text{--H}_2\text{O}$.

This possibility was revealed by the results contained in papers [11, 12] on the experimental research and theoretical modeling of the processes of deposition of ZnS and $\text{ZnO}_x\text{S}_{1-x}$ from aqueous-organic solutions of complex composition. The authors proposed to use a series of the most reliable values of constants of the formation of eight amino- and hydroxocomplexes of zinc in the temperature range of 25–90 °C.

Similar tools, but taking into consideration mixed amine-hydroxocomplexes, were later used by the authors of papers [13, 14] to simulate the process of the interaction of Zn_2SiO_4 with ammonia and saline solutions. In addition to the distribution of zinc atoms among various complex ions, the authors also calculated and experimentally proved the existence in the solution of the SOA with the polymerization degree from 1 to 4. Thus, the possibility of mathematical modeling of the composition of multi-component solutions containing a sufficiently wide range of different silicate- and zinc-containing ions was shown. However, given the high degrees of polymerization of SOA in the ZAWG, the approach based on the discrete MMD model of SOA cannot be considered to be suitable for the quantitative description of the system under consideration.

3. The aim and objectives of the study

The aim of this work is to explain the existence of a rheological anomaly in the ZAWG by complicating and expanding the capabilities of the previously developed mathematical model with the inclusion in consideration of the MCS solutions, in addition to the AMS solutions.

To achieve this aim, the following tasks had to be solved:

– to modify the theoretical model of the silicate solution used in paper [8] and to optimize the process of convergence of the iterative procedure;

– to show the possibility of mathematical modeling of a rheological anomaly in the solutions of the AS and the MCS (in the particular case of ZAWG) and its absence in the solutions of AS and TAS;

– to test the possibilities of computation with the use of the modified model not only of the average MMD parameters of the SOA, but also of concentrations of different structural types of cations and anions.

4. Calculation model: accounting for the entire system of zinc-containing complex ions

The calculation model proposed in this paper was created by modifying the model used in paper [8] and was based on the same three assumptions. The introduced changes make it possible to expand significantly the scope of its application, including in consideration the MCS solutions as well. The main object of the description of the modified model was the ZAWG as the most complex system to be described.

Like for any silicate solutions, the most important thermodynamic introductory parameters of the model are the equilibrium constants of the following processes:

– dissociation of silanol groups:

$$K_a = \frac{[\equiv \text{Si}-\text{O}^-] \times [\text{H}^+]}{[\equiv \text{Si}-\text{OH}]}, \quad (2)$$

– polycondensation of SOA:

$$K_p = \frac{[\equiv \text{Si}-\text{O}-\text{Si} \equiv] \times [\text{OH}^-]}{[\equiv \text{Si}-\text{OH}] \times [\equiv \text{Si}-\text{O}^-]}, \quad (3)$$

– protonation of weak bases:

$$K_b = \frac{[\text{R}-\text{NH}_3^+] \times [\text{OH}^-]}{[\text{R}-\text{NH}_2]}, \quad (4)$$

– dissociation of water:

$$K_w = [\text{H}^+] \times [\text{OH}^-]. \quad (5)$$

In the case of ZAWG, ammonia is a weak base and in equation (4) $R=H$.

To describe the solutions of MCS, it is necessary to take into account the constant of instability of complex ions. In particular, for the ZAWG were taken into consideration the cumulative instability constants of four ammino complexes:

$$[\text{Zn}(\text{NH}_3)]^{2+} K_{a1} = \frac{[\text{Zn}^{2+}] \times [\text{NH}_3]}{[\text{Zn}(\text{NH}_3)^{2+}]}, \quad (6)$$

$$[\text{Zn}(\text{NH}_3)_2]^{2+} K_{a2} = \frac{[\text{Zn}^{2+}] \times [\text{NH}_3]^2}{[\text{Zn}(\text{NH}_3)_2^{2+}]}, \quad (7)$$

$$[\text{Zn}(\text{NH}_3)_3]^{2+} K_{a3} = \frac{[\text{Zn}^{2+}] \times [\text{NH}_3]^3}{[\text{Zn}(\text{NH}_3)_3^{2+}]}, \quad (8)$$

$$[\text{Zn}(\text{NH}_3)_4]^{2+} K_{a4} = \frac{[\text{Zn}^{2+}] \times [\text{NH}_3]^4}{[\text{Zn}(\text{NH}_3)_4^{2+}]}, \quad (9)$$

and of four hydroxo complexes:

$$[\text{Zn}(\text{OH})]^+ K_{h1} = \frac{[\text{Zn}^{2+}] \times [\text{OH}^-]}{[\text{Zn}(\text{OH})^+]}, \quad (10)$$

$$[\text{Zn}(\text{OH})_2] K_{h2} = \frac{[\text{Zn}^{2+}] \times [\text{OH}^-]^2}{[\text{Zn}(\text{OH})_2]}, \quad (11)$$

$$[\text{Zn}(\text{OH})_3]^- K_{h3} = \frac{[\text{Zn}^{2+}] \times [\text{OH}^-]^3}{[\text{Zn}(\text{OH})_3^-]}, \quad (12)$$

$$[\text{Zn}(\text{OH})_4]^{2-} K_{h4} = \frac{[\text{Zn}^{2+}] \times [\text{OH}^-]^4}{[\text{Zn}(\text{OH})_4^{2-}]}. \quad (13)$$

For stoichiometry considerations, four more equations are obtained:

$$4C_{\text{Si}} = [\equiv \text{Si}-\text{OH}] + [\equiv \text{Si}-\text{O}^-] + 2[\equiv \text{Si}-\text{O}-\text{Si} \equiv], \quad (14)$$

$$C_{\text{N}} = [\text{NH}_3] + [\text{NH}_4^+] + [\text{Zn}(\text{NH}_3)^{2+}] + 2[\text{Zn}(\text{NH}_3)_2^{2+}] + 3[\text{Zn}(\text{NH}_3)_3^{2+}] + 4[\text{Zn}(\text{NH}_3)_4^{2+}], \quad (15)$$

$$C_{\text{Zn}} = [\text{Zn}^{2+}] + [\text{Zn}(\text{NH}_3)^{2+}] + [\text{Zn}(\text{NH}_3)_2^{2+}] + [\text{Zn}(\text{NH}_3)_3^{2+}] + [\text{Zn}(\text{NH}_3)_4^{2+}] + [\text{Zn}(\text{OH})^+] + [\text{Zn}(\text{OH})_2] + [\text{Zn}(\text{OH})_3^-] + [\text{Zn}(\text{OH})_4^{2-}], \quad (16)$$

$$[\text{OH}^-] + [\equiv \text{Si}-\text{O}^-] + [\text{Zn}(\text{OH})_3^-] + 2[\text{Zn}(\text{OH})_4^{2-}] = [\text{H}^+] + C_{\text{Na}} + [\text{NH}_4^+] + 2[\text{Zn}^{2+}] + 2[\text{Zn}(\text{NH}_3)^{2+}] + 2[\text{Zn}(\text{NH}_3)_2^{2+}] + 2[\text{Zn}(\text{NH}_3)_3^{2+}] + 2[\text{Zn}(\text{NH}_3)_4^{2+}] + [\text{Zn}(\text{OH})^+], \quad (17)$$

where C_{Si} , C_{N} , C_{Zn} and C_{Na} are the total molar concentrations of silica, ammonia, zinc and sodium in the solution.

In this research, like in papers [6, 8], the magnitude of the SOA (x) was used to characterize the degree of polymerization of SOA. Basicity is linearly related to the commonly used magnitude of connectivity of the SOA (Q) by the ratio: $x=2-0.5Q$ and is particularly convenient to characterize highly polymerized silicate structures. Magnitude x can vary from 0.0 (crystal quartz, polymerization degree is equal to infinity) up to 2.0 (orthosilicate acid, degree of polymer-

ization is equal to one). The average magnitude of basicity of the SOA in the system can be written down through the concentration of siloxane bonds and total molar concentration of silica in the solution:

$$x = 2 - [\equiv \text{Si} - \text{O} - \text{Si} \equiv] / C_{\text{Si}} \tag{18}$$

The resulting system of equations (2)–(18) was solved by the Newton method, designed to solve the systems of non-linear equations, and was implemented with the help of a specially designed computer program SISCALC-9 in the programming language C++. Similarly to papers [8, 15], all the input parameters and the unknown variables, except for the parameters of the original composition of the solution and x values participated in the equations in logarithmic form in order to improve the accuracy and stability of the solution.

Thus, the set of input parameters consists of the magnitudes of total molar concentrations of silica, sodium, zinc and nitrogen, as well as decimal logarithms of constants of equilibrium, which appear in equations (2) to (13), the total of 16 magnitudes. The set of variables is a set of decimal logarithms of current concentrations of ions and silicate structures, which appear in equations (2) to (18), including pH and pOH values, as well as the average basicity of the SOA, the total of 17 magnitudes. The final form of the equation system is: 17 equations, of which 12 are linear and 5 are nonlinear.

In the process of calculation, the Jacobians were calculated after each iteration. The iterative process was terminated after the magnitude of a change in pH that was less than 0.0001 was achieved. Less than thirty iterations were needed to achieve the required accuracy in all cases. The zero approximations of variables were set by mean values of actually permissible intervals.

The magnitudes of equilibrium constants for different temperatures were calculated using a special SILSOL sub-program through calculating by the van 't Hoff isotherm equation. In this case, experimental or assumed values of enthalpy changes in reactions of water dissociation (ΔH_w), dissociation of silanol group (ΔH_a), protonation of ammonia (ΔH_b) and polycondensation of the SOA (ΔH_p) were used. As for the constants of instability of complex ions, their values in the temperature range of 25–90 °C were borrowed from publication [12].

5. Results of calculating the parameters of MMD of SOA and concentrations of silicate- and zinc-containing structures

5.1. Selection of values for input parameters

The system of equations (2)–(18) by the SISCALC-9 program was solved for the ZAWG of different compositions, having practical importance for obtaining water resistant insulation in the temperature range from +25 to +90 °C (298–363 K). In this case, for the indicators of equilibrium constants and enthalpies, we used commonly acceptable values ($pK_w=14.0$, $\Delta H_w=55.8$ kJ/mol, $pK_b=4.74$, $\Delta H_b=51.4$ kJ/mol) or substantiated earlier [8, 16, 17] intervals of values ($pK_a=10.6–11.5$, $\Delta H_a=40–90$ kJ/mol, $pK_p=1.0–2.0$, $\Delta H_p=10–25$ kJ/mol). The values of indicators of constants of instability of complex ions, used in calculations, are shown in Table 1.

Table 1

Values of instability constants for zinc-containing complexes [12] used in calculations in SISCALC-9 program

T, K	Ammino complexes				Hydroxo complexes			
	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}	pK_{h1}	pK_{h2}	pK_{h3}	pK_{h4}
298	2.43	4.92	7.83	9.26	6.26	10.22	14.39	16.51
303	2.40	4.85	7.63	9.09	6.29	10.17	14.23	15.42
313	2.34	4.72	7.26	8.76	6.35	10.09	13.96	15.07
323	2.30	4.59	6.95	8.43	6.42	10.04	13.74	14.79
333	2.26	4.47	6.68	8.10	6.51	10.03	13.58	14.57
343	2.23	4.36	6.44	7.78	6.61	10.04	13.45	14.40
353	2.21	4.25	6.25	7.47	6.72	10.08	13.37	14.27
363	2.20	4.15	6.08	7.15	6.83	10.14	13.32	14.18

It follows from the data shown in Table 1 that:

- a) at all temperatures, hydroxocomplexes are stronger than the corresponding ammine complexes;
- b) stability of all ammine complexes decreases when heated, while among hydroxocomplexes, only three- and tetrahydrozincates behave in this way. Two other hydroxocomplexes demonstrate hardening when heated or non-monotonous temperature dependence.

5.2. Determining the dependence of structural indicators of solutions on their composition

The equation of chemical reaction (1), which reflects the total process of the formation of ZAWG, correctly describes the process of interaction of the mixture of water glass and ammonia with small portions of ZnO. Despite the above-mentioned advantage of the stability of zinc hydroxocomplexes over ammonia complexes, the latter are first to be formed on condition that $[\text{NH}_3] \gg [\text{OH}^-]$.

Fig. 2 shows the graph of the calculated change in values of x and pH in the process of dissolving ZnO in the mixture of aqueous solutions of sodium water glass and ammonia at $T=298$ K ($C_{\text{Si}}=2.0$, $C_{\text{N}}=2.0$, $C_{\text{Na}}=1.33$, $pK_a=11.0$, $pK_p=1.2$). The initial region of an increase of both curves corresponds to the process of formation of zinc ammonia complex by reaction (1). It is accompanied by an increase in pH and, as a result, depolymerization of SOA (increased value of x). The ratio $[\text{NH}_3]/[\text{OH}^-]$ at this stage of the process varies from 316 to 110.

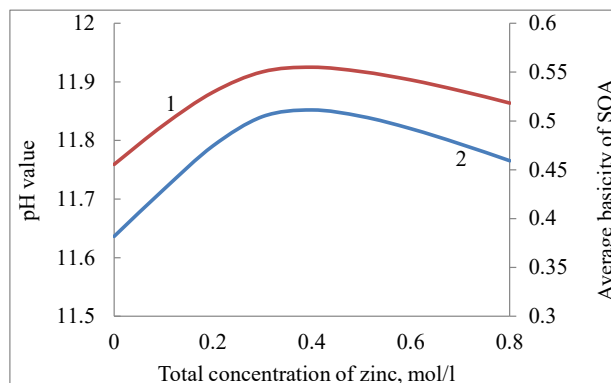
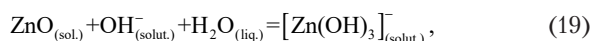


Fig. 2. Change in the basicity of SOA (curve 1) and magnitude pH (curve 2) depending on zinc concentration in the solution

After $C_{\text{Zn}} > 0.4$, the character of the curves changes from increasing at the rise in C_{Zn} to decreasing. Ratio

$[\text{NH}_3]/[\text{OH}^-]$ at this stage of the process changes from 90 to 65, ratio $[\text{Zn}(\text{NH}_3)_4^{2+}]/[\text{Zn}(\text{OH})_3^-]$ – from 4.0 to 1.0. Therefore, at this stage, reaction (1) as the main one is replaced by another.



which passes at a decrease in pH, and consequently, with the shift of the MMD of SOA towards polycondensation, that is with a decrease in the x value and an increase in the viscosity of the solution.

Calculation dependences of x and pH on C_{Zn} have the same character at all other temperatures in the studied range as well. The corresponding curves pass through maximum at the values of argument from 0.1 ($pK_a=10.6$, $\Delta H_a=40$, $pK_p=1.0$, $\Delta H_p=25$, $T=363$) to 0.5 ($pK_a=10.6$, $\Delta H_a=90$, $pK_p=1.0$, $\Delta H_p=10$, $T=363$). Calculations show that an increase in maximum on the curves is shifted to the left at an increase in T and ΔH_p , as well as at a decrease in ΔH_a .

5. 3. Determining the temperature dependence of the structural characteristics of solutions

Based on the data from Table 1, it can be logically assumed that the effect of the temperature increase in the nature of the change in x value in solutions of ZAWG should be qualitatively the same as the effect of the growth of C_{Zn} at constant temperature. This means that one should expect a negative dependence of x on T , at least in the range of medium to high temperatures. The calculation proves this assumption.

As an example, Table 2 shows the calculated values of the most important structural parameters of the diluted ($C_{\text{Si}}=2$) solution of ZAWG in comparison with the characteristics of the original silicate-ammonia solution, which does not contain zinc. The results of the calculation for the two temperatures, the minimum and the maximum, in the studied temperature interval are shown. The values of the enthalpy parameters are: $\Delta H_a=40$ kJ/mol, $\Delta H_p=25$ kJ/mol.

Table 2

Calculated structural characteristics of aqueous solutions $\text{Na}_2\text{O}\cdot 3\text{SiO}_2\cdot 2\text{NH}_3$ and $\text{Na}_2\text{O}\cdot 3\text{SiO}_2\cdot 2\text{NH}_3\cdot 0.5\text{ZnO}$ at 298 K and 363 K

pK_a	pK_p	T , K	x	$[\equiv\text{Si}-\text{O}-\text{Si}\equiv]/C_{\text{Si}}$	$[\text{Zn}(\text{NH}_3)_4^{2+}]/[\text{Zn}(\text{OH})_3^-]$	pOH
$\text{Na}_2\text{O}\cdot 3\text{SiO}_2\cdot 2\text{NH}_3$						
10.6	1.0	298	0.362	2.45	–	2.33
		363	0.350	2.52	–	1.67
11.0	1.2	298	0.390	2.42	–	2.23
		363	0.370	2.50	–	1.57
11.5	2.0	298	0.572	2.14	–	2.35
		363	0.514	2.27	–	1.70
$\text{Na}_2\text{O}\cdot 3\text{SiO}_2\cdot 2\text{NH}_3\cdot 0.5\text{ZnO}$						
10.6	1.0	298	0.499	1.59	2.67	2.16
		363	0.321	2.81	0.42	1.72
11.0	1.2	298	0.511	1.63	2.31	2.07
		363	0.322	3.02	0.34	1.65
11.5	2.0	298	0.702	1.37	2.75	2.18
		363	0.491	2.48	0.45	1.73

It is easy to see that an increase in the degree of polymerization of SOA (a decrease in x value) occurs in both

zinc-containing and zinc-free systems (in the latter – due to the existence of a weak base of NH_3). However, in the zinc-containing system, this effect is by order of magnitude stronger, which is why it can explain the existence of a rheological anomaly. It should be noted that the close relationship between the viscosity of silicate solutions and the parameters of the MMD of SOA was pointed out by many authors, including recent publications [18].

The following parameter – the number of siloxane bonds, which falls on one silicon atom – behaves accordingly. While in the zinc-free system it is weakly dependent on temperature, in the ZALG it increases sharply (on average, by 1.8 times) when heated from 25 °C to 90 °C.

The next parameter is the ratio of concentrations of amino and hydroxo complex ions, which are most widely presented in the solution. This parameter is the most important for understanding chemical processes at heating ZAWG. It is evident that its magnitude significantly (on average by 6.4 times) decreases during heating from 25 °C to 90 °C. The reason for this phenomenon has already been discussed above. It is the difference of the values of enthalpy of decomposition of these two types of zinc complexes.

The dependence of magnitudes of basicity of the SOA on temperature for the same two systems at $pK_a=10.6$, $pK_p=1.0$ and four sets of enthalpy parameters is shown in Fig. 3. It is easy to notice that the rate of a decrease in x value at the rise in temperature (and therefore, intensity of a rheological anomaly) increases at an increase in ΔH_p and decreases at an increase ΔH_a . That is why, in particular, of the four calculations of the ZAWG examined in Fig. 3 (continuous curves), only three indicate the existence of a rheological anomaly. The fourth calculation with the most unfavorable set of the enthalpy parameters (the continuous curve of the blue color), excludes this possibility.

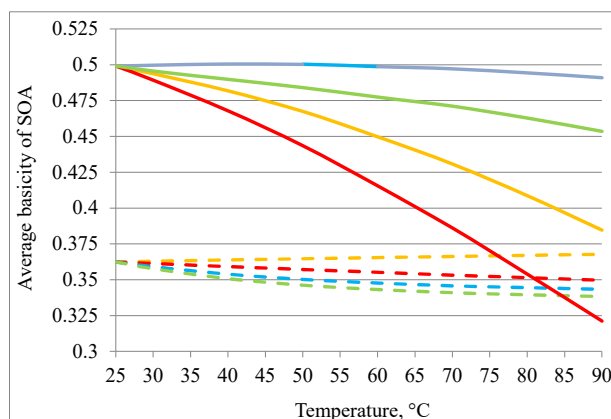


Fig. 3. Temperature dependence of average basicity of the SOA in the solution at $pK_a=10.6$ and $pK_p=1.0$. Broken lines: $C_{\text{Zn}}=0$; continuous lines: $C_{\text{Zn}}=0.5$. Enthalpy parameters (ΔH_a and ΔH_p , in kJ/mol): orange color – 40, 10; red color – 40, 25; blue color – 90, 10; green color – 90, 25

As for non-zinc silicate-ammonia solutions, the calculation also shows a monotonous decrease in x value at an increase in temperature for some of them. The examples are the red, blue and green broken curves in Fig. 3. However, the magnitude of the relative decrease x in the studied temperature interval is by order of magnitude lower than that of the ZAWG. This is consistent with the experimentally established fact that there is no rheological anomaly in systems $\text{Na}_2\text{O} - \text{SiO}_2 - \text{NH}_3 - \text{H}_2\text{O}$.

6. Discussion of results from modeling the properties of aqueous solutions of silicates with complex cations

The calculation model proposed here assumes a complete accounting of the balance of all zinc-containing complex ions, which allows self-consistent modeling of the structure and properties of the ZAWG. However, in order to understand the chemical aspect of the processes of the formation of the ZAWG and its thermal evolution, it is necessary to identify the key formations in the solution that determine its physical and chemical properties.

Fig. 4 shows the graph of the evolution of zinc distribution among ion-molecular formations in the process of disintegration of ZnO in the silicate-ammonia solution. The graph shows the molar fractions of particles, the concentration of which in the solution exceeds 0.01 M at least at one point of the studied range of C_{Zn} .

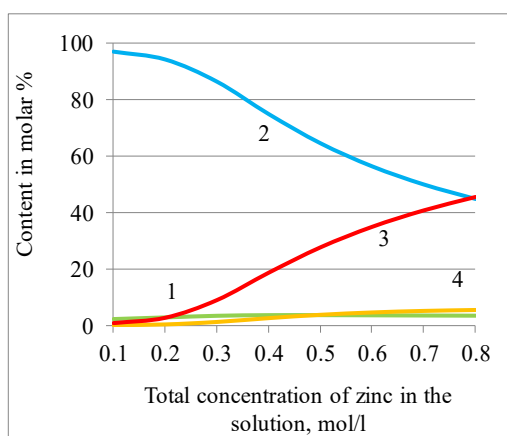


Fig. 4. The content of various zinc-containing ions in silicate solution (in molar % of the total content of zinc): 1 – $[Zn(NH_3)_3]^{2+}$, 2 – $[Zn(NH_3)_4]^{2+}$, 3 – $[Zn(OH)_3]$, 4 – $[Zn(OH)_4]^{2-}$

It is easy to see that in the entire range of C_{Zn} , more than 90 % of Zn atoms exist in the solution in the form of cations $[Zn(NH_3)_3]^{2+}$ and anions $[Zn(OH)_3]$. These ions, along with sodium cations, polysilicate anions and ammonia molecules, crucially determine the physical and chemical properties of the ZAWG. This explains the appropriateness of using chemical equations (1) and (19) to describe the reaction of the formation of the ZAWG under different conditions.

Similar patterns can be detected in the analysis of the evolution of zinc distribution between complex ions in the process of heating ZAWG. As an example, Fig. 5 shows a graph of a change in such distribution for aqueous solution $Na_2O \cdot 3SiO_2 \cdot 2NH_3 \cdot 0.5ZnO$ ($C_{Zn}=2.0$, $pK_a=10.6$, $\Delta H_a=40$, $pK_p=1.0$, $\Delta H_p=25$). It can be seen that two ionic forms alternately dominates in the solution: at $T < 65^\circ C$ – $[Zn(NH_3)_4]^{2+}$, above this temperature – $[Zn(OH)_3]$.

It should be taken into consideration that the chemical process described in Fig. 5, occurs with constant chemical composition of the solution and cannot correspond to equations (1) or (2). Here, there is a typical re-complexing reaction, that is, zinc redistribution between different complex ions. Disregarding the existence of all complex ions with low concentration, including those described by curves 1, 3 and 5, we obtain the following equation of the reaction that determines the chemical nature of the process:

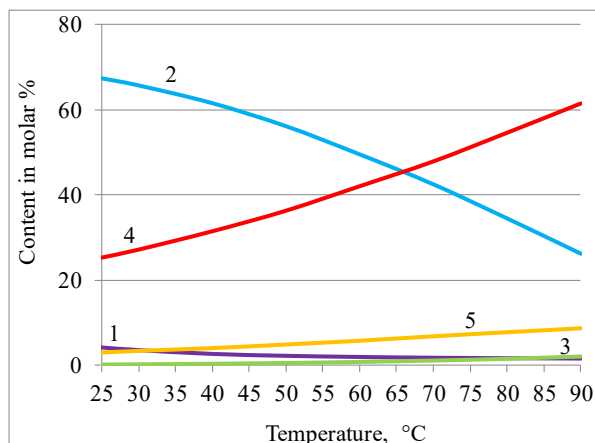
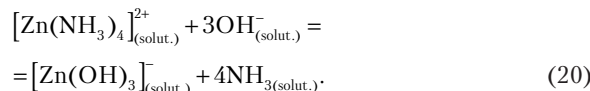


Fig. 5. Temperature dependence of zinc distribution in various forms: 1 – $[Zn(NH_3)_3]^{2+}$, 2 – $[Zn(NH_3)_4]^{2+}$, 3 – $Zn(OH)_2$, 4 – $[Zn(OH)_3]$, 5 – $[Zn(OH)_4]^{2-}$

Similarly to reaction (19), this process leads to a decrease in the pH magnitude, and therefore to an increase in the polycondensation of SOA and an increase in viscosity of the solution. It is safe to say that reaction (20) is responsible for the appearance of a rheological anomaly in the ZAWG.

The only difficult thing in the description of the ZAWG with the help of the proposed model was that in many cases, the calculated product $[Zn^{2+}][OH^-]^2$ significantly exceeds the magnitude of the product of solubility $Zn(OH)_2$ (K_{sp}). According to [12], magnitude pK_{sp} in the studied temperature range takes the values from 15.79 to 16.49. This contradiction should be resolved in the course of further research, especially since in practice the ZAWG demonstrates absolute stability. Sedimentation of $Zn(OH)_2$ is not observed even in the area of rheological anomaly. Perhaps the reason for the increased solubility of $Zn(OH)_2$ in silicate solutions is the formation of zinc-silicate complexes, the existence of which in alkaline-silicate solutions was reported in paper [19].

An important merit of the proposed model and the SISCALC-9 computer program is the possibility of using them to quantify the water solutions of other WSS. In particular, to model the solutions of other MCS, it is enough to modify equations (6) to (13) with a possible change in their quantity, as well as of equations (4) and (15) to (17). To model solutions of non-silicate systems with complex ions, it will also be necessary to modify equations (2), (3), as well as (14) and (18). Finally, to model the solutions of AS and TAS, it is enough to reset to zero input parameters C_N and C_{Zn} in the original version of SISCALC-9, parameters C_{Na} и C_{Zn} , in the case of AS solutions, only C_{Zn} in the case of mixtures of AS and AMS. Thus, it is possible to calculate the parameters of the MMD of SOA for a wide range of aqueous solutions of WSS and analyze the possibility of a rheological anomaly existing in them.

It is obvious that the rheological anomaly in the system studied here exists due to a specific combination of thermodynamic properties of zinc complexes. Neverthe-

less, it is possible to formulate a qualitative criterion for the possibility of the occurrence of a rheological anomaly in the solutions of the MSC by the mechanism proposed in this paper:

– fairly small magnitudes of indicators of constants of instability of the hydroxocomplex and cation complex (ammino, ethylenediamine complexes, etc.), to ensure good solubility of the oxide or hydroxide;

– advantage of magnitudes of pK of instability of hydroxo complexes over magnitudes of pK of cation complexes (at least for a pair of the most stable complexes of both types);

– advantage of magnitudes ΔH of decomposition of cation complexes over magnitudes ΔH of decomposition of hydroxo complexes.

In this regard, the following systems seem promising regarding the rheological anomaly: $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{N}(\text{C}_2\text{H}_4)\text{NH}_2-\text{ZnO}-\text{H}_2\text{O}$, $\text{H}_2\text{N}(\text{C}_2\text{H}_4)\text{NH}_2-\text{SiO}_2-\text{ZnO}-\text{H}_2\text{O}$ and, probably, some other. In general, there can not be many such systems, unlike AMS with rheological anomaly.

Among the theoretical problems that need to be resolved, the main problem is the explanation of the existence of a rheological anomaly in lithium silicate solutions. Given the high exothermic nature of the reaction of hydration of lithium cation, the mathematical model of lithium silicate solution should take into consideration the equilibrium of the formation of aqua-complexes, similar to the model used in this research. It is possible that the description of the rheological anomaly in this system will require further complication of the model, in particular, taking into consideration activity coefficients of ions.

7. Conclusions

1. The modification of the previously used mathematical model of aqueous silicate solution was proposed in order to include in consideration solutions of metal-complex silicates. The subject of modeling, first of all, was sodium silicate water glass, modified with zinc and ammonia

(ZAWG), used to produce water-resistant insulation. The input parameters of the model are: concentrations of silica, silicate-forming cation, metal-complexing agent, complexing agent, constants of equilibrium of the process of dissociation of water and silanolic group, of polycondensation of the latter and of decomposition of complex ions, as well as changes in enthalpy during the same processes. Application of the modified model to the ZAWG leads to the system of seventeen linear and nonlinear equations, numerically solved by the Newton method. The solution makes it possible to determine the most important parameters of the MMD of SOA in the solution, pH value and the concentration of complex cations and anions. Due to the full accounting of the ion composition of the solution, the model is applicable to describe aqueous solutions of any water-soluble silicates and their mixtures.

2. With the help of the modified calculation model, the experimentally observable effect of the rheological anomaly in the ZAWG, which is the positive temperature dependence of viscosity of the solution, was explained. It was shown that the cause of the anomaly is the same as in amino silicate solutions – the shift of molecular weight equilibrium of silicate-oxygen anions towards polycondensation. This shift, in turn, is explained by the re-complexing of zinc-containing ions at an increase in temperature. The zinc ammonia complexes mainly transfer to hydroxocomplexes due to enthalpy of decomposition of the latter that is smaller by magnitude. It was shown that a similar process also occurs when the ZAWG is obtained from water glass, zinc oxide and aqueous ammonia. For both processes, the graphs of evolution of zinc distribution among different types of ions were plotted.

3. The assumptions about the possible existence of a rheological anomaly in solutions of other metal-complex silicates were put forward, the qualitative criterion for the search of such systems was formulated. It was concluded that the rheological anomaly in the ZAWG is explained by a special combination of thermodynamic properties of complex zinc ions and is hardly widespread among metal-complex silicates.

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