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THE RHEOLOGICAL ANOMALY IN WATER-SILICATE SYSTEMS: A POSSIBLE THERMODYNAMIC EXPLANATION

N. Maliavski
PhD, Associate Professor
Department of general chemistry
National Research University Moscow
State University of Civil Engineering
Yaroslavskoye highway, 26, Moscow, Russia, 129337
E-mail: nikmal08@yandex.ru
O. Zhuravlova
PhD, Deputy Director
Corporation «SIIG»
Volodimira Monomaha str., 25-a/2,
Dnipro, Ukraine, 49000
E-mail: ol.ig.zh@gmail.com
O. Denysiuk
PhD, Assistant
Department of information systems
Ukrainian State University of Chemical Technology
Gagarina ave., 8, Dnipro, Ukraine, 49005
E-mail: denolga91@rambler.ru

З метою теоретичного моделювання ефекту реологічної аномалії у водних розчинах аміносилікатів пропонується проста математична модель для розрахунку полімеризаційних та кислотно-основних рівноваг у водних розчинах силікатів аліфатичних амінів та силікатів лужних металів. Модель дозволяє пояснити існування аномалії у розчинах силікатів амінів та відсутність її у розчинах лужних силікатів

Ключові слова: розчинні силікати, силікати амінів, водні розчини, аномальна реологія, терможелатинізація, поліконденсація

С целью теоретического моделирования эффекта реологической аномалии в водных растворах аминосиликатов предлагается простая математическая модель для расчета полимеризационных и кислотно-основных равновесий в водных растворах силикатов алифатических аминов и силикатов щелочных металлов. Модель позволяет объяснить существование аномалии в растворах силикатов аминов и отсутствие ее в растворах щелочных силикатов

Ключевые слова: растворимые силикаты, силикаты аминов, водные растворы, аномальная реология, терможелатинизация, поликонденсация

1. Introduction

Aminosilicate (AS) solutions are aqueous solutions of polysilicates of aliphatic, alicyclic or heterocyclic amines as well as amino alcohols and other amino compounds. They may be obtained by ion exchange from alkali silicates or by direct dissolution of solid silicic acid in aqueous solutions of compounds with a sufficiently high basicity constant of amino or imino groups ($K_b>10^{-4.5}$).

The properties of such solutions are largely determined by two interrelated equilibria, namely, the amine ionization equilibrium and the polycondensation equilibrium of the silicon-oxygen anions (SOA). Resulting pH values and parameters of the molecular mass distribution (MMD) of silicate anions are determined by the amine type, amine and silica concentrations and the temperature. The most interesting property of aqueous solutions of AS is that all solutions, sufficiently concentrated in silica, exhibit the effect of a rheological anomaly, or thermogelation. The effect consists in a reversible increase in the viscosity of the solution with increasing temperature, up to gelation of the solution.

Although more than 20 years have passed since the discovery of the rheological anomaly in AS solutions, the physicochemical mechanism of the phenomenon is still not completely established.

2. Literature review and problem statement

For the first time, the effect of a rheological anomaly in solutions of AS was reported in 1994 [1], and it was immediately noted and in subsequent works confirmed that thickening of solutions with heating is accompanied by an increase in the average degree of the SOA polymerization [2, 3]. A similar effect was observed in other silicate systems, namely in aqueous solutions of lithium silicates [4] and sodium – tetramminezinc silicate [5]), as well as in several non-silicate organic systems. The latter include aqueous solutions of methylcellulose [6, 7], of hydroxypropyl methylcellulose [6, 8], of some block copolymers based on polyalkylene glycols, N-substituted polyacrylamides, polyphosphazenes, etc. [9, 10]. However, in all these cases the anomaly has a completely different mechanism that is not associated with the polymerization of ions [6, 9, 11].

In Table 1, the first descriptions of the most important liquid systems, exhibiting the rheological anomaly, are listed in chronological order.

Table 1

Known to date systems with the rheological anomaly

System	Year of discovery and authors	Anomaly mechanism
Aqueous solutions of lithium silicates	1907 (J. M. Ordway)	The inverse temperature dependence of the solubility of lithium silicates in water
Aqueous solutions of methylcellulose	1935 (E. Heymann)	Enhancement of the hydrophobic attraction of polymeric chains due to the dehydration with increasing temperature
Liquid sulfur	1943 (R. F. Bacon, R. Fanelli)	Reversible polymerization upon heating to 159 °C
Aqueous solutions of copolymers based on polyalkylen glycols, etc.	1972 (I. Schmolka)	Micellar aggregation caused by enhanced hydrophobic interaction due to a decrease in the degree of hydration of polar groups with increasing temperature
Aqueous solutions of aminosilicates	1994 (N. Maliavski et al.)	Increase in the polymerization degree of SOA with increasing temperature

It should be noted that despite the lack of a sufficiently reliable theoretical explanation of the effect in any system that demonstrates it, the phenomenon itself has become practical, in particular, in ceramic production when casting ceramic gels with methylcellulose as a thickener [12–14], as well as in medicine [15].

It was also reliably established that solutions of silicates of strong bases (alkali metals, except lithium [16, 17], and quaternary ammonium bases [11]) do not exhibit the rheological anomaly. As an example, in Fig. 1 the dependences of the decimal logarithm of dynamic viscosity (η, mPa·s) on temperature are shown for several water-silicate and water-borate systems exhibiting and not exhibiting the rheological anomaly [2, 11].

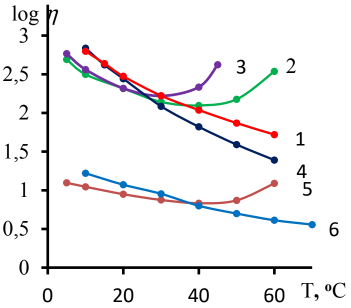


Fig. 1. Temperature dependence of logη for the aqueous solutions (numbers in parentheses are the values of molar silicate or borate module): 1 – Na silicate (2.9), 2 – Li silicate (3.0), 3 – piperidine silicate (2.8), 4 – diethyl-bis(2-hydroxypropyl)ammonium silicate (1.5), 5 – ethanolamine silicate (0.57), 6 – ethanolamine borate (1.3)

It is easy to see that only the curves corresponding to the silicates of medium (curve 3) and weak (curve 5) bases as well as lithium silicate (curve 2), show a significant anomaly, which consists in the increase in viscosity with increasing temperature in a fairly wide temperature range (20 °C and more). This effect is absolutely reversible: viscosity changes follow temperature changes in both directions, the backlog does not exceed 10 minutes [2]. In the low-temperature region, however, all the systems exhibit a normal rheological behavior, i. e. a decrease in viscosity with increasing temperature.

As for water-silicate systems, there is a high probability that for a qualitative and semi-quantitative explanation of the rheological anomaly in them it is sufficient to take into account only acid-base and polymerization equilibria in such solutions. The state of the problem of theoretical modeling aqueous solutions of silicates at the end of the 1970s is described in monograph [4], where the dissociation constants of a mono-, oligo- and polysilicic acids and the polycondensation constant of monosilicate ions, are given. This line of research was further developed in a number of works, the authors of which created theoretical models based on the results of potentiometric [18], NMR [18, 19], rheological [20], FTIR [21] and other experiments. In all these studies, the equilibrium between monomeric and individual oligomeric SOA was studied with the use of experimental or calculated data on the corresponding equilibrium constants.

On the other hand, the authors of paper [22] successfully used the assumption of the independence of polycondensation equilibrium parameters on the structure and size of polysilicate anions for the modeling of silicate solutions. Based on this assumption, they showed the possibility of calculating the average degree of polymerization of SOA in aqueous solutions of alkaline silicates and aminosilicates using only two input parameters: the silica concentration and the pH value.

3. The aim and objectives of the study

The aim of this work is to theoretically explain the occurrence of the rheological anomaly in AS solutions by the thermodynamic factor, namely, the positive dependence of the equilibrium degree of SOA polymerization on temperature.

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

– to construct a simple mathematical model of interrelated acid-base and polycondensation equilibria in AS solutions;

– to check the developed model for adequacy, i. e. for the ability to correctly describe the response of SOA MMD to changes in system parameters;

– to check the ability of the model to explain the fact that the rheological anomaly exists in aqueous solutions of AS, but does not exist in aqueous solutions of silicates of strong bases.

4. The method of theoretical modeling

The present paper is a development of the approach used earlier in paper [22] used towards estimation of average degrees of the SOA polymerization in solutions and pH values using only two experimental values uniquely determined by chemical compositions of the prepared solutions (the silica concentration and the molar silicate module). The proposed calculation model is based on the following assumptions:

– aqueous solutions of aminosilicates, as well as other soluble silicates, are of an equilibrium nature;

– the dynamic viscosity of silicate solutions is directly related to the average degree of polymerization of the SOA;

– the values of the dissociation constant of the silanol groups of the SOA and the equilibrium constants of the polycondensation process of the SOA do not depend on the type of anion and its degree of polymerization.

Of these assumptions, the first two ones are based on the totality of the results of experimental studies of AS solutions, and the third one is a perfectly permissible simplification, which greatly facilitates the calculation and does not qualitatively change its results.

The properties of AS solutions are determined to a great extent by two interrelated equilibria: the amine ionization equilibrium and the polycondensation equilibrium of silicate anions:

$$-\mathrm{NH_2}+\mathrm{H_2O} \leftrightarrow -\mathrm{NH_3^+}+\mathrm{OH^-}, \tag{1}$$

$$\mathrm{H}_p\mathrm{Si}_m\mathrm{O}_q^{-x}+\mathrm{H_3SiO_4^-} \leftrightarrow \mathrm{H}_{p+2}\mathrm{Si}_{m+1}\mathrm{O}_{q+3}^{-x}+\mathrm{OH^-}. \tag{2}$$

The higher the value of the amine basicity constant (K_b), the stronger the equilibrium (1) is shifted to the right, and the equilibrium (2) – to the left, towards the less polymerized SOA. Increasing the total concentration of SiO_2 in the solution, on the contrary, shifts the equilibrium (2) to the right.

Then we have three chemical equilibria, which determine the ionic composition of the solution, with the constants, respectively, of the silanol bond dissociation (K_a), of the amine protonation (K_b) and of the SOA polycondensation (K_p):

$$\equiv\mathrm{Si-OH} \leftrightarrow \equiv\mathrm{Si-O^-}+\mathrm{H^+}, \tag{3}$$

$$K_a=\frac{[\equiv\mathrm{Si-O^-}]\times[\mathrm{H^+}]}{[\equiv\mathrm{Si-OH}]}, \tag{4}$$

$$\mathrm{R-NH_2}+\mathrm{H_2O} \leftrightarrow \mathrm{R-NH_3^+}+\mathrm{OH^-}, \tag{5}$$

$$K_b=\frac{[\mathrm{R-NH_3{}^+}]\times[\mathrm{OH^-}]}{[\mathrm{R-NH_2}]}, \tag{6}$$

$$\equiv\mathrm{Si-OH}+\equiv\mathrm{Si-O^-} \leftrightarrow \equiv \mathit{S}\mathrm{i-O-Si}\equiv+\mathrm{OH^-}, \tag{7}$$

$$K_p=\frac{[\equiv\mathrm{Si-O-Si}\equiv]\times[\mathrm{OH^-}]}{[\equiv\mathrm{Si-OH}]\times[\equiv\mathrm{Si-O^-}]}. \tag{8}$$

On the basis of stoichiometry, we have three more dependencies:

$$4\mathrm{C_{SiO_2}}=[\equiv\mathrm{Si-OH}]+[\equiv\mathrm{Si-O^-}]+2[\equiv\mathrm{Si-O-Si}\equiv], \tag{9}$$

$$\mathrm{C_{RNH_2}}=[\mathrm{R-NH_3^+}]+[\mathrm{R-NH_2}], \tag{10}$$

$$[\equiv\mathrm{Si-O^-}]+[\mathrm{OH^-}]=[\mathrm{R-NH_3^+}], \tag{11}$$

where $\mathrm{C_{SiO_2}}$ and $\mathrm{C_{RNH_2}}$ denote the total molar concentrations of silica and amine in the solution. Moreover, in the last equation, we considered it permissible to neglect the concentration of hydrogen cations, taking into account a substantially alkaline medium in the silicate solutions at practically important concentrations (pH=10.5–12.5).

To assess a degree of "cross-linking" of silicate anions structure, we used a basicity value x that is the molar ratio H_2O/SiO_2 in the molecule of the corresponding silicic acid. The basicity is most convenient for the characterization of highly polymerized silicates and is related to the more frequently used SOA connectivity value (Q) by the relation $Q=4-2x$. In our case, the mass-average basicity of the SOA may be expressed in terms of the system parameters used here as follows:

$$x=2-[\equiv\mathrm{Si-O-Si}\equiv]/\mathrm{C_{SiO_2}}. \tag{12}$$

Finally, we have one more interrelation of concentrations – the ionic product for water:

$$K_w=[\mathrm{H^+}]\times[\mathrm{OH^-}]. \tag{13}$$

Thus, a system of eight equations (4), (6), (8) and (9)–(13) is obtained. Four of these equations are nonlinear. This model can also be used to calculate the equilibria in solutions of alkali silicates and silicates of quaternary ammonium bases – by using the assumption of complete ionization of the cation (equilibrium (5) is completely shifted to the right).

Taking into account the substitutions, the solution of the system is reduced to solving the following equation:

$$Q\left(F+\frac{K_w}{K_a}\right)-2x\sqrt{\mathrm{C_{SiO_2}}}=0, \tag{14}$$

where the values of the parameters Q and F, respectively, are equal to:

$$Q=\sqrt{\frac{(2-x)K_a}{K_pK_w}},$$

$$F=\frac{K_b}{2}\left(\sqrt{1+\frac{4\mathrm{C_{RNH_2}}}{K_b\left(1+Q\sqrt{\mathrm{C_{SiO_2}}}\right)}}-1\right).$$

The solution is facilitated by the fact that in the only range of basicity $0 \le x \le 2$ that has a physical meaning, the equation always has a solution and moreover a unique one.

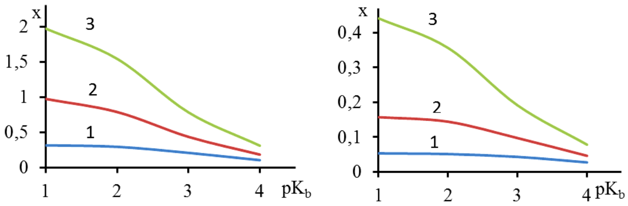
5. The results of the calculations

The solution of equation (14) with respect to x for different values of the total concentrations of amine and silica was carried out numerically by the half-division method. For the standard temperature of 298 K we used the conventional values of the constants: pK_w=14.0; pK_a=9.8 [4]; pK_p=0.86 [4]; the pK_b values for the amines were taken from monograph [23]. For the solutions of silicates of the strong bases, the suppositive value $pK_b=-3$ was used, which almost completely eliminates the possibility of hydrolysis over the cation.

5. 1. Adequacy of the model

The results of calculations performed for concentrated solutions of amine (methylamine, diethylamine, piperidine, ethylenediamine, ethanolamine, guanidine etc.) and sodium silicates give quite reasonable, albeit somewhat understated, values of the mass-average basicity of the SOA. Thus, for the solutions with silica concentrations 10–20 % by weight and silicate modules 2–3, x values lying in the ranges 0.1–0.3 (aminosilicates) and 0.3–0.5 (sodium silicates) are found, which is in a satisfactory agreement with the majority of experimental data obtained by the methods of molybdate spectrophotometric analysis and NMR on Si-29 nuclei [1, 4].

In addition, the calculation results reproduce the experimentally established [4, 22] dependences of the x value on the parameters of the solution composition. The main of these dependences is an increase of x value with increasing C_{RNH_2} at constant C_{SiO_2}, with decreasing C_{SiO_2} at constant C_{RNH_2} and with decreasing value of amine's pK_b at constant C_{RNH_2} and C_{SiO_2}. This is confirmed by Fig. 2, where the curves x=F(pK_b) calculated according to formula (22), are shown for several values of C_{SiO_2} and C_{RNH_2}.



a *b*

Fig. 2. Calculated dependencies of the average SOA basicity x on the amine's pK_b value. The silica molar concentration: *a* – 0.5, *b* – 2.0; the amine molar concentration: 1 – 0.3; 2 – 1.0; 3 – 3.0

A less trivial dependence is also reproduced, namely, a dependence of x value on C_{SiO_2} at a constant silicate module. In complete agreement with experimental data [1, 4], we obtain a significant increase in x value with decreasing C_{SiO_2} for AS and a very weak dependence for alkali silicates.

Some other experimentally observed effects in solutions of silicates cannot be explained using this model, at least, at the existing level of its complexity. Such effects include, for example, the non-monotonic dependence of average SOA basicity on amine concentration at a constant silica concentration and the value of x=2 in saturated aqueous solutions of silica. There is reason to hope that these effects can also be reproduced in a qualitative or semi-quantitative way on the basis of the proposed model, for example, by taking into account real activity coefficients of ions, by including H^+ cations to equation (11), and also by allowing the dependence of the dissociation constant of the silanol group on degrees of polymerization and ionization of the silicate anions.

5. 2. Temperature dependencies of SOA basicity

The temperature dependence of the average SOA basicity was calculated for both types of silicate solutions: aminosilicates and silicates of the strong bases. The pK_b values for the amines at temperatures from 0 °C to +100 °C, were determined using the published thermodynamic data [23]. For alkali silicates and other silicates of strong bases, the value of the protonation enthalpy was assumed to be zero because the temperature changes in the suppositive pK_b value cannot affect the calculation results.

To calculate pK_a and pK_p values, due to the lack of reliable experimental data, we used various sets of values of enthalpy of silanol dissociation ΔH_a and of SOA polymerization ΔH_p within some physically meaningful intervals. Typical examples of the calculation results are given in Table 2. The values 51.4 kJ/mol and –8.3 kJ/mol, which are respectively the highest estimate for ΔH_a value and the lowest estimate for ΔH_p value, were calculated from the data given in monograph [4].

Table 2

Average SOA basicity values for the solutions of methylamine and sodium silicates at C_{SiO_2}=2 calculated for three temperatures and eight sets of thermodynamic parameters

No.	Enthalpy, kJ/mol			$(CH_3NH_3)_2O{\cdot}2.8SiO_2$			$Na_2O{\cdot}2.8SiO_2$		
	ΔH_a	ΔH_b	ΔH_p	0 °C	25 °C	60 °C	0 °C	25 °C	60 °C
1	0	0	0	0.194	0.141	0.117	0.360	0.366	0.389
2	0	0.8	0	0.192	0.141	0.118	0.360	0.366	0.389
3	0	0.8	–8.3	0.182	0.141	0.131	0.360	0.366	0.394
4	0	0.8	10	0.203	0.141	0.104	0.361	0.366	0.380
5	25	0.8	–8.3	0.158	0.141	0.136	0.361	0.366	0.378
6	51.4	0.8	–8.3	0.136	0.141	0.153	0.363	0.366	0.369
7	51.4	0.8	0	0.145	0.141	0.141	0.365	0.366	0.366
8	51.4	0.8	10	0.157	0.141	0.128	0.367	0.366	0.364

Similar results were obtained for silicates of other amino compounds and other strong bases (potassium, tetramethylammonium, diethyl-bis(2-hydroxypropyl)ammonium silicates).

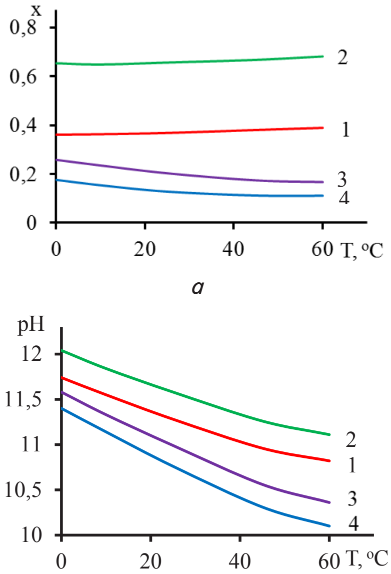
6. Discussion of results of modeling the rheological anomaly

As follows from the results presented in Table 2, for a typical AS solution in all cases except one (line 6) we observe an increase in the degree of polymerization (or, which is the same, a decrease in the average basicity of the SOA), with increasing temperature. At the same time, for solutions of silicates of strong bases, such as sodium silicate, in all cases, an inverse relationship is observed: a decrease in the degree of polymerization (an increase in the basicity of the SOA) with increasing temperature.

The obtained results on the MMD displacement of the SOA are consistent with the different steepness of the calculated curves of the pH temperature dependence: for the solutions of AS, the rate of decrease in pH with increasing temperature is noticeably higher than for the solutions of alkali silicates. As an example, in Fig. 3 the temperature dependences of x and pH values are shown for the solutions of silicates of methylamine (MA), piperidine (PPN), sodium (Na) and tetramethylammonium (TMA) with equal silica concentrations (2.0 mol/l), calculated using the same set of the enthalpy variables corresponding to No. 1 in Table 2.

With increasing temperature, the concentration of hydroxide ions increases mainly because of the intensification of the water dissociation process. The same applies to the temperature dependence of the $[OH^-]$ value in the sodium silicate solution, but there we observe, on the contrary, the depolymerization of the SOA upon heating, although very weak. Such a result can be explained by a change in the form of the first term inside the brackets in equation (14): at large values of K_b, it ceases to depend on K_w, and hence on temperature, and the temperature dependence of x becomes determined by the second term inside the brackets, which ensures a total positive temperature dependence of SOA basicity.

In general, for solutions of aminosilicates exhibiting a rheological anomaly, the results of calculations lead to the following conclusions: the intensity of the rheological anomaly should increase with increasing values of C_{RNH_2} and ΔH_p, as well as the silicate module, and decreasing values of C_{SiO_2}, ΔH_a and ΔH_b. As for the dependence of the effect intensity on the value of amine's pK_b, it is non-monotonic, passing through a maximum between pK_b=2 and pK_b=3.5. The effect intensity is evaluated here as $I_{r.a.}=(x_1-x_2)/x_1$ (where $T_1<T_2$).



a

b

Fig. 3. Calculated temperature dependencies for silicate solutions: *a* — of the average SOA basicity *x*; *b* — of the pH value. Cations: 1 — Na; 2 — TMA; 3 — PPN; 4 — MA. Molar silicate modules: 1 — 2.8; 2 — 1.5; 3 — 2.8; 4 — 2.8

Table 3 shows the calculated parameters of the rheological anomaly effect for solutions of several silicates ($M_2O{\cdot}nSiO_2$) with various values of pK_b. The compositions of compared solutions correspond to maximum values of silica solubility, that is, such solutions are the most stable for every given amine compound.

Table 3

Parameters of the rheological anomaly effect calculated for silicate solutions at temperatures 0–100 °C

No.	Cation name	pK_b	$[SiO_2]$	[M]	$I_{r.a.}$	Anomaly region, °C
1	Ammonium	4.8	0.08	3.0	0.27	0–55
2	Ethanolammonium	4.5	1.7	3.0	0.18	0–40
3	Trimethylammonium	4.2	1.9	3.0	0.23	0–45
4	Methylammonium	3.4	4.0	3.0	0.29	0–65
5	Piperidinium	2.8	4.0	3.0	0.30	0–85
6	Hexamethylenediammonium	2.1	3.5	3.0	0.25	0–100
7	Guanidinium	1.5	5.0	3.0	0.07	0–85
8	Sodium	(–3)	6.7	4.7	no	no

The data displayed in Table 3 confirm the above conclusion regarding the dependence of the anomaly intensity on the amine basicity. The probability of the existence of the anomaly in solutions of ammonium and guanidinium silicates is not high. In the first case, this is hampered by a low concentration of silica in the solution, in the second case – a small calculated value of $I_{r.a.}$. However, this does not exclude the possibility of experimental detection of the rheological anomaly in solutions whose compositions are close to boundaries of a system stability region.

Analysis of the results obtained in this paper, suggests that a significant rheological anomaly capable of leading to a thermogelation at temperatures below 100 °C, can be observed in aminosilicate solutions with a calculated value of $I_{r.a.}$ above 0.1, standard (at 298 K) average SOA basicity below 0.5–0.75, and the silica content higher than 1 wt. %. Such solutions can be readily prepared by dissolving solid polysilicic acid in aqueous 3–4 M solutions of amine compounds with pK_b of the amino group 2.0–4.5. The existence of solutions with the rheological anomaly in non-silicate systems, for example, in aminoborate, aminoaluminate or aminophosphate ones seems also possible.

7. Conclusions

1. To explain the rheological anomaly in aqueous solutions of aminosilicates, a simple mathematical model of interrelated acid-base and polycondesation equilibria in such solutions was constructed. The proposed calculation model assumes a direct dependence of the solution viscosity on the polymerization degree of silicate anions, as well as the independence of the dissociation constant of silanol groups and the polycondensation equilibrium constant on the degree of anions polymerization.
2. The proposed model allows calculating the pH values and the average basicity of silicate anions, closed to those found experimentally. It also correctly reproduces displacements of the molecular mass distribution of silicate anions under the influence of changes in the chemical composition and the concentration of solutions. Some other, less trivial experimentally observed effects in solutions of silicates cannot be explained using this model, at least, at the existing level of its complexity.
3. The results of calculations using the proposed model, confirm the presence of a positive temperature dependence of the polymerization degree of silicate anions in the aminosilicate solutions, in contrast to the solutions of silicates of the strong bases. Thus, the proposed mathematical model of polymerization-hydrolysis equilibria in aqueous silicate solutions qualitatively explains the existence of the rheological anomaly in aqueous solutions of aminosilicates and its absence in solutions of alkali silicates and silicates of quaternary ammonium bases.

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