

Simulation of Molecular Mass Distributions and Evaluation of O^{2-} Concentrations in Polymerized Silicate Melts

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Received January 12, 2007

Abstract—A new statistical model is proposed for the molecular mass distributions (MMD) of polymerized anions in silicate melts. The model is based on the known distribution of Q^n species in the MeO–Me₂O–SiO₂ system. In this model, chain and ring complexes are regarded as a random series of Q^n structons with various concentrations of bridging bonds ($1 \leq n \leq 4$, Q^0 corresponds to SiO₄⁴⁻). This approach makes it possible to estimate the probability of formation of various ensembles of polymer species corresponding to the general formula (Si_iO_{3i+1-j})^{2(i+1-j)-}, where i is the size of the ion, and j is the cyclization number of intrachain bonds. The statistical model is utilized in the STRUCTON computer model, which makes use of the Monte Carlo method and is intended for the calculation of the composition and proportions of polyanions at a specified degree of polymerization of silicate melts (STRUCTON, version 1.2; 2007). Using this program, we simulated 1200 MMD for polyanions in the range of $0.52 \leq p \leq 98$, where p is the fraction of nonbridging bonds in the silicon–oxygen matrix. The average number of types of anions in this range was determined to increase from three (SiO₄⁴⁻, Si₂O₇⁶⁻, and Si₃O₁₀⁸⁻) to 153, and their average size increases from 1 to 7.2. A special option of the STRUCTON program combines MMD reconstructions in silicate melts with the formalism of the Toop–Samis model, which enables the calculation of the mole fraction of the O^{2-} ion relative to all anions in melts of specified composition. It is demonstrated that, with regard for the distribution and average size of anion complexes, the concentration of the O^{2-} ion in the MeO–SiO₂ system is characterized by two extrema: a minimum at 40–45 mol % SiO₂, which corresponds to the initial stages of the gellenization of the polycondensated silicate matrix, and a maximum, which is predicted for the range of 60–80 mol % SiO₂.

DOI: 10.1134/S0016702908050017

INTRODUCTION

Progress in modern techniques for genetic interpretations of magmatic rocks is related to the development of computer models for phase equilibria in silicate systems consisting of a melt and crystals. The calibration basis of such models is provided by experimental data on the melting of rocks and their synthetic analogues, and mathematical basis of the models is systems of empirical equations describing distributions of components between solid phases and melts. Assuming thermodynamic equilibrium between the phases, these equations can be written in the form of dependences of the free energy of the system, or the distribution constants, on the composition and P - T parameters. This makes it possible to simulate the successive melting and crystallization of natural silicate melts using methods of direct [1] or “implicit” [2] minimization of the thermodynamic potentials at a specified bulk composition of the system. The MELTS [3, 4] and COMAGMAT [5, 6]

software program packages are now widely applied in magmatic petrology to conduct a diversity of genetic reconstructions (see reviews [7–9]). At the same time, some disadvantages of these programs, which became obvious at the turn of this century, cannot be eliminated by varying some input parameters. These problems involve the settling of oxide phases, simulation of peritectic relations (first of all, for *Ol* and *Opx*), the effect of volatile components, and the simulation of high-pressure equilibria. This is partly accounted for by the ambiguity of experimental data and difficulties in making them mutually consistent, but the main problem is still the choice of components and thermodynamic model for the magmatic melt. Here some avenues were proposed for developing the ion–polymer theory for the structure of silicate melts with regard for the tendencies in the distribution of polymer components of various sizes depending on the SiO₂ concentration. The effect of other network-forming components (such as Al and Ti) still cannot be taken into account.

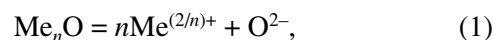
METHODS FOR THE THERMODYNAMIC DESCRIPTION OF SILICATE MELTS

The two principal means for the selection of components for describing the mixing properties of a silicate liquid are as follows [10]. In the stoichiometric approach, a solution is considered that corresponds to a certain number of chemical compounds. The compositions of the thermodynamic components and species are thereby identical and can be written as simple (SiO_2 and MgO), multiple (Si_4O_8), or complex (CaSiO_3 and Mg_2SiO_4) oxides. This simplifies the formalism and calibration of the mixing parameters of the oxide systems within the scope of the theory of regular solutions (see, for example, [11]). This ideology was applied in [12] to model magmatic melts based on multiple oxides and compounds having the same chemical formulae as minerals. The changes introduced with time into the component basis of the MELTS program made it possible to somewhat expand the applicability field of this model at preserving the principle of equal numbers of components and species [4, 9].

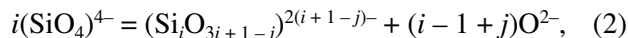
An alternative approach, which is developed in the chemistry of glass-forming melts, is underlain by so-called speciation models, in which the existence of species ensembles is admitted, with the numbers of these ensembles greater than the number of the components used to describe the chemical composition of the system. In formulating such models, it is implied that silicate complexes (molecular associates) can form in melts, with these complexes occurring in reversible chemical equilibria and being subject to the mass action law. It is thereby necessary to evaluate the equilibrium distribution of components in the melts, which further complicates the description of the system by means of the theory of associated solutions [13, 14]. These methods are well adjusted for the simulation of simple alkali-silicate and silicate-borate systems [15, 16] and binary and triple melts characterizing metal cinders (for example, [17]).

The theory of associated solutions has not, however, received wide recognition and application in the physical chemistry of magmatic processes. In their petrological simulations, researchers mostly rely onto the aforementioned semiempirical crystallization models in which the melt is viewed as a mixture of arbitrarily selected components, which do not, however, occur among the actual species of the silicate melt, such as SiO_2 and NaAlO_2 [5, 18, 19] or Fe_2O_3 and Na_2SiO_3 [4]. Obviously, the utilization of such molecular species makes it difficult to apply the computer simulation models to the whole compositional ranges of silicate systems and the accurate enough reproduction of phase relations, including liquid immiscibility in silica-rich regions.

An alternative approach used in the thermodynamics of magmatic melts is the application of ion-polymer models, which take into account the dissociation of oxides in melts



and the possibility of polycondensation of silicon-oxygen complexes with the origin of high-dimension chain-ring structures



where i is the size of a polyanion (the number of Si atoms in it), and j is the number of closures (cyclization) of its intrachain (cyclic) bonds [20]. These reactions form chains ($j=0$) and a diversity of "ring" structures ($j \geq 1$). Thus, each act of the polycondensation of the chains and cyclization of the anions produces in Si-O⁰-Si bridging bonds (of a doubly bonded O⁰ atom) and an O²⁻ ion from two end-positioned (singly bonded, nonbridging) oxygen atoms



The forms of the reactions determined the differences between the chemical (2) and quasichemical (3) approaches to the description of the polycondensation of silicate melts, but their shared feature is the assumption of equilibrium between the finite number of polymer species (nonbridging and bridging oxygen atoms) and the low-molecular product, the O²⁻ ion. The concentration (activity) of free oxygen ions O²⁻ is an indicator of the basicity of the melt [21] and is important for the calculations of the activities of components for constructing melting [22, 23] and many other diagrams.

The amount of O²⁻ ions in systems of given composition is usually estimated from the mass and charge balance, including nonbridging O⁻ and bridging O⁰ atoms [24]. The proportions of these virtual atoms defines the overall degree of polymerization of the silicon-oxygen matrix (the completeness of polycondensation reactions), the statistical average proportions of quasichemical structural units, and the probable size distribution of the chemical complexes. Attempts to calculate these distributions were undertaken with the use of statistical modeling techniques [25–27] and semiempirical models for anion equilibria that were proposed to describe linear and branched chains [28–30], predominant linear-ring structures [31], and various complex compounds [32], including isomer forms [20, 33, 34]. The problem of evaluating the relative concentrations of polymers (which is known in the physical chemistry of polymers as the calculation of molecular-mass distributions MMD) [35] is complicated by the necessity for accounting for the gelization of the silicate liquid, a process expected in $\text{Me}_n\text{O-SiO}_2$ systems near metasilicate melts [36]. The gelization process proceeds via forming infinite branched and self-cycling polymer chains, which form an interrelated framework of silicon-oxygen tetrahedrons with enrichment in SiO_2 (i.e., an increase in the O⁰/O⁻ ratio).

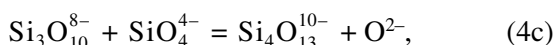
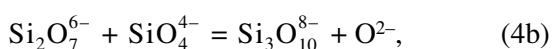
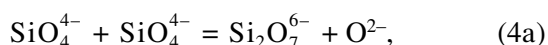
Difficulties in describing such processes in molten silicates were one of the main reasons why the theory and calculations of polyanion equilibria are practically not applied in the simulation of magmatic processes.

The evaluation of MMD within broad ranges of SiO₂ concentrations remained an unsolved problem [13] and is much less popular than instrumental methods for studying the structure of quenched glasses and melts [37, 41]. Nevertheless, several researchers continue to develop simulation techniques for polyanion equilibria and the valuation of activities of free oxygen ions in cinder-forming systems [23, 42–45]. The past years witnessed attempts to apply these approaches in experimental and theoretical petrology, including the description of Fe³⁺/Fe²⁺ redox equilibria [46] and S solubility [47, 48] in silicate liquids. Potentiometric methods are developed in application to melts with the aim of direct determination of the activity of the O²⁻ ion and the examination of its effect on the activity coefficients of oxides of transition metals [49–52]. Interesting attempts were undertaken to parameterize water solubility depending on the experimentally measured concentration of free oxygen ions in binary cinders [45].

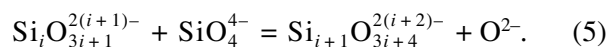
Obviously, more advanced ion-polymer models may facilitate further progress in the description of phase equilibrium and the properties of silicate melts within broad compositional ranges typical of cinder-forming and magmatic systems [53, 54]. This paper represents a new approach to evaluating the MMD of polymer complexes and simulating anion equilibria in low and moderately polymerized melts (see also [55]).

MMD SIMULATIONS FOR SILICATE MELTS

In order to justify the proposed approach, it is expedient to consider the basic principles used to describe polymerized silicate melts. The process of melt polycondensation with the development of linear chains and branched isomers is usually rendered as a succession of reactions



or, in a more general form, as



Here the reactants and reaction products are silicate complexes able to elongate the chains via forming Si–O⁻ bonds at nonbridging oxygen atoms, which compose the SiO₄⁴⁻ radical and are predominant among the polyanions. The ability of the chains to form cycles (the process of cyclization) is also predetermined by the interaction of singly bound oxygen atoms within the same chain anion [20, 34]

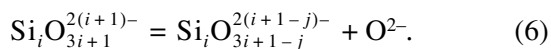


Table 1 lists some potentially possible polymer species corresponding to general formula (2) for rela-

tively small anions with $1 \leq i \leq 10$ and cyclization index $0 \leq j \leq 7$. Formally, this massif may be infinitely extended, but the actual number of stable complexes is finite, because cyclization is constrained to the maximum possible length of the chains, and the successive increase in the size of the partly cyclized ring structures results in a decrease in the overall amount of polymer molecules. Furthermore, it should also be taken into account that the sharing of an edge of two silicon–oxygen tetrahedrons (i.e., connection via two pairs of end bonds) or, particularly, the sharing of a face of two tetrahedrons, is hardly probable in polymerization reactions [20, 32, 34]. This puts forth the problem of the identification and calculation of the proportion of polymers stable in silicate melts of given composition.

This problem should be successively solved because, if the ensemble of polyanions is realistically selected and their relative proportions are accurately evaluated, the bulk of the free dissolution energy of the melt may be attributed to the mechanical and configuration mixing terms of silicate complexes. This makes it possible to proceed from the terms of excess entropy of mixing in the form of a product of the Margules parameters (in models of regular solutions for “mineral-like” components, see above) to expressions including the theoretically predicted or instrumentally estimated mole fractions of species [10]. These models are formulated with regard for the fact that the energy threshold of cation substitution for anions is high, and the probability of the random mixing of positively and negatively charged ions is close to zero [27]. Hence, the integral effect of the dissolution of oxides and deviations from ideality in silicate melts can be described with regard for the configuration effects of the “ideal” mixing of ions in two independent matrixes: cationic (modifiers) and anionic (network). This allows us to utilize relatively simple expressions for the activities of mineral-forming components in melts, which may be evaluated within broad compositional ranges by the method proposed for melts of ion salts [56].

For metal oxides in binary [24, 28, 26] and more complicated [46, 47] melts, this approach leads to the equations

$$a_{\text{MeO}}^l = a_{\text{Me}^{2+}}^l a_{\text{O}^{2-}}^l, \quad (7)$$

$$a_{\text{Me}^{2+}}^l = x_{\text{Me}^{2+}}^l = n_{\text{Me}^{2+}} / \Sigma \text{ cations}, \quad (8a)$$

$$a_{\text{O}^{2-}}^l = x_{\text{O}^{2-}}^l = n_{\text{O}^{2-}} / \Sigma \text{ anions}, \quad (8b)$$

where a_{MeO}^l , $a_{\text{Me}^{2+}}^l$ and $a_{\text{O}^{2-}}^l$ are the activities of oxide, metal ion, and O²⁻, respectively, and $x_{\text{Me}^{2+}}^l$, and $x_{\text{O}^{2-}}^l$ are the concentrations of the metal ion among the cations (Σ cations is the amount of positively charged ions) and the O²⁻ ion in the anion matrix (Σ anions is the sum of

Table 1. Potentially possible forms of chain ($j = 0$) and ring ($j \geq 1$) silicate complexes according to Eq. (2)

i	$j = 0$	$j = 1$	$j = 2$	$j = 3$	$j = 4$	$j = 5$	$j = 6$	$j = 7$
1	$\boxed{\text{Si}_2\text{O}_4^{4-}}$							
2	$\boxed{\text{Si}_2\text{O}_7^{6-}}$	$\rightarrow \text{Si}_2\text{O}_6^{4-}$	$\rightarrow \text{Si}_2\text{O}_5^{2-}$	$\rightarrow \text{Si}_2\text{O}_4$				
3	$\boxed{\text{Si}_3\text{O}_{10}^{8-}}$	$\rightarrow \text{Si}_3\text{O}_9^{6-}$	$\rightarrow \text{Si}_3\text{O}_8^{4-}$	$\rightarrow \text{Si}_3\text{O}_7^{2-}$	$\rightarrow \text{Si}_3\text{O}_6$			
4	$\boxed{\text{Si}_4\text{O}_{13}^{10-}}$	$\rightarrow \text{Si}_4\text{O}_{12}^{8-}$	$\rightarrow \text{Si}_4\text{O}_{11}^{6-}$	$\rightarrow \text{Si}_4\text{O}_{10}^{4-}$	$\rightarrow \text{Si}_4\text{O}_9^{2-}$	$\rightarrow \text{Si}_4\text{O}_8$		
5	$\boxed{\text{Si}_5\text{O}_{16}^{12-}}$	$\rightarrow \text{Si}_5\text{O}_{15}^{10-}$	$\rightarrow \text{Si}_5\text{O}_{14}^{8-}$	$\rightarrow \text{Si}_5\text{O}_{13}^{6-}$	$\rightarrow \text{Si}_5\text{O}_{12}^{4-}$	$\rightarrow \text{Si}_5\text{O}_{11}^{2-}$	$\rightarrow \text{Si}_5\text{O}_{10}$	
6	$\boxed{\text{Si}_6\text{O}_{19}^{14-}}$	$\rightarrow \boxed{\text{Si}_6\text{O}_{18}^{12-}}$	$\rightarrow \text{Si}_6\text{O}_{17}^{10-}$	$\rightarrow \text{Si}_6\text{O}_{16}^{8-}$	$\rightarrow \text{Si}_6\text{O}_{15}^{6-}$	$\rightarrow \text{Si}_6\text{O}_{14}^{4-}$	$\rightarrow \text{Si}_6\text{O}_{13}^{2-}$	$\rightarrow \text{Si}_6\text{O}_{12}$
7	$\boxed{\text{Si}_7\text{O}_{22}^{16-}}$	$\rightarrow \boxed{\text{Si}_7\text{O}_{21}^{14-}}$	$\rightarrow \text{Si}_7\text{O}_{20}^{12-}$	$\rightarrow \text{Si}_7\text{O}_{19}^{10-}$	$\rightarrow \text{Si}_7\text{O}_{18}^{8-}$	$\rightarrow \text{Si}_7\text{O}_{17}^{6-}$	$\rightarrow \text{Si}_7\text{O}_{16}^{4-}$	$\rightarrow \text{Si}_7\text{O}_{15}^{2-}$
8	$\boxed{\text{Si}_8\text{O}_{25}^{18-}}$	$\rightarrow \boxed{\text{Si}_8\text{O}_{24}^{16-}}$	$\rightarrow \boxed{\text{Si}_8\text{O}_{23}^{14-}}$	$\rightarrow \text{Si}_8\text{O}_{22}^{12-}$	$\rightarrow \text{Si}_8\text{O}_{21}^{10-}$	$\rightarrow \text{Si}_8\text{O}_{20}^{8-}$	$\rightarrow \text{Si}_8\text{O}_{19}^{6-}$	$\rightarrow \text{Si}_8\text{O}_{18}^{4-}$
9	$\boxed{\text{Si}_9\text{O}_{28}^{21-}}$	$\rightarrow \boxed{\text{Si}_9\text{O}_{27}^{18-}}$	$\rightarrow \boxed{\text{Si}_9\text{O}_{26}^{16-}}$	$\rightarrow \text{Si}_9\text{O}_{25}^{14-}$	$\rightarrow \text{Si}_9\text{O}_{24}^{12-}$	$\rightarrow \text{Si}_9\text{O}_{23}^{10-}$	$\rightarrow \text{Si}_9\text{O}_{22}^{8-}$	$\rightarrow \text{Si}_9\text{O}_{21}^{6-}$
10	$\boxed{\text{Si}_{10}\text{O}_{31}^{24-}}$	$\rightarrow \boxed{\text{Si}_{10}\text{O}_{30}^{20-}}$	$\rightarrow \boxed{\text{Si}_{10}\text{O}_{29}^{18-}}$	$\rightarrow \boxed{\text{Si}_{10}\text{O}_{28}^{16-}}$	$\rightarrow \text{Si}_{10}\text{O}_{27}^{14-}$	$\rightarrow \text{Si}_{10}\text{O}_{26}^{12-}$	$\rightarrow \text{Si}_{10}\text{O}_{25}^{10-}$	$\rightarrow \text{Si}_{10}\text{O}_{24}^{8-}$

Note: i is the size of the anion, and j is the cyclization number of "free" bonds of nonbridging oxygen atoms. The cyclization direction according to reaction (6) is indicated by arrows. Boxes indicate "stable" complexes [20, 52, 60].

negatively charged species), and $n_{\text{Me}^{2+}}^l$ and $n_{\text{O}^{2-}}^l$ are the amounts of the metal and free oxygen ions.

The expressions for the activities of silicate end members acquire terms with the concentrations of silicon–oxygen species participating in the corresponding mineral-forming reactions. For example, for Mg and Fe orthosilicates (the *Fo–Fa* system), with regard for the ionic nature and stoichiometry of the interacting components [57, 58],



we obtain

$$a_{Ol}^l = (a_{\text{Me}^{2+}}^l)^2 a_{\text{SiO}_4}^l, \quad (10)$$

where

$$a_{\text{SiO}_4}^l = x_{\text{SiO}_4}^l = n_{\text{SiO}_4} / \Sigma \text{ anions}. \quad (11)$$

It is easy to calculate the fraction of modifiers in the cation matrix, and the main problems encountered in the application of relations (7)–(8) and (10)–(11) are the evaluation of the O^{2-} and SiO_4^{4-} concentrations. Inasmuch as the monomer participates in polycondensation reaction (2), the problem of summation of the amounts of polyanions and free oxygen ions becomes crucial

$$\Sigma \text{ anions} = \Sigma \text{Si-anions} + n_{\text{O}^{2-}}. \quad (12)$$

Esin's models. In the late 1970s, this problem was actively attacked by Esin [20, 33, 34, 59, 61], who developed principles for the construction of an ion-polymer model combining the statistical evaluation of the isomer species for branched chains [29, 30] and approaches to the description of ring complexes regardless of isomerization [32]. The model was underlain by the calculation of the distribution of “all possible” polymerized anions by the modified Bernoulli equation [30]

$$x_{i,j} = \omega_{i,j} (1-p)^{(i-1+j)} p^{(2i+1-2j)} (1-x_{\text{O}^{2-}}^l), \quad (13)$$

where $x_{i,j}$ is the mole fraction of an anion complex consisting of i atoms of Si, which were formed by the polycondensation of nonbridging bonds by reaction (5) and include j intramolecular cyclized nonbridging bonds according to reaction (6); $\omega_{i,j}$ is a factorial term, which is calculated by the formula

$$\omega_{i,j} = (3i-j)! / [(2i+1-2j)!(i+j)!], \quad (14)$$

$1-p$ is the probability of the formation of a bridging bond, which is determined through the functionality of monomer f ($f=4$ for the SiO_4^{4-} ion) and the parameter α as

$$1-p = 0.5\alpha f / (f-1) = 2\alpha/3, \quad (15)$$

characterizing the progress of the polycondensation reaction [30]

$$\alpha = 2n_{\text{O}^{2-}} / (2n_{\text{O}^{2-}} + n_{\text{O}^{2-}}), \quad (16)$$

where $n_{\text{O}^{2-}}$ and n_{O^-} are the numbers of bridging and single-bond oxygen atoms in one mole of the silicate melt. These values are related to the molecular mass distribution (13) via the simple relations [20]:

$$n_{\text{O}^{2-}} = \Sigma \Sigma (i-1+j)x_{i,j} (\Sigma \text{Si-anions} + n_{\text{O}^{2-}}) \quad (17)$$

and

$$n_{\text{O}^-} = 2\Sigma \Sigma (i+1-j)x_{i,j} (\Sigma \text{Si-anions} + n_{\text{O}^{2-}}). \quad (18)$$

Summation over i and j is conducted for linear and stable tridymite-like ring complexes (starting with $\text{Si}_6\text{O}_{18}^{12-}$, Table 1), whose possible ensemble is specified by the equation for the minimum size of the anions i_{min} at a given j value [32]

$$j = i_{\text{min}} + 1 - 1.71(i_{\text{min}})^{2/3}. \quad (19)$$

Supplementing these relations with constraints imposed by the mass balance of the components and the law of mass action for reaction (4a) forming the dimer, Esin managed to close the system of equations (13)–(19) and proposed an algorithm for its solution by the method of successive iterations [20, 34]. The principal difficulties encountered in the solution of this system were related to the calculation of high-dimensional factorials (14) and the necessity for summation in the iteration cycles of the corresponding $\Sigma \Sigma x_{i,j} = \Sigma \text{Si-anions}$, $\Sigma \Sigma i x_{i,j}$, and $\Sigma \Sigma j x_{i,j}$ series (17), (18). This algorithm could first be utilized in the mid-1970s, when BESM-6 computers appeared. Because of the significant duration of the calculations for an “infinite” ensemble of species ($i \rightarrow \infty, j \rightarrow \infty$), only a few results were obtained that characterized the concentration of the O^{2-} ion (MeO activity) at concentrations of 50 and 61 mol % SiO_2 for the PbO–SiO_2 , MnO–SiO_2 , FeO–SiO_2 , and SnO–SiO_2 binary systems [60]. No complete information on the MMD of the anions was reported. The disadvantages of this approach are evidently related to the rigidly specified selection of the anion ensemble and the main postulate of the Masson–Whiteway model, according to which, in constructing a general polymerization scheme, one of the four nonbridging bonds of the SiO_4^{4-} monomer is recorded (see comments in [14]). This condition predetermines the further calculation of the probability of the formation of polymer species of various geometry and size, and it was proved inaccurate for silicate complexes [62].

Estimating MMD by the method of statistical simulations. A more coherent approach that is independent of the assumed polycondensation scheme was proposed in [25]. This approach is underlain by the postulate of a random distribution of end-positioned oxygen atoms in a polymerized silicon–oxygen matrix. This assumption largely follows from the concepts that polymerization and/or polycondensation reactions (2) characterize a dynamic equilibrium in which polymer complexes are formed and decompose over a time span

during which this equilibrium is reached [63]. Lacy [25] was the first to estimate MMD in silicate melts based on the probability of the formation of a bridging bond, which was evaluated as $1 - p$, where p is the average fraction of singly bonded oxygen atoms among the four oxygen atoms coordinating one silicon atom

$$p = n_{O^-} / (2n_{O^0} + n_{O^-}) = 2(R - 2) / 4, \quad (20)$$

$R = \Sigma O / Si$ is the oxygen/silicon ratio in the polymerized matrix ($\Sigma O = n_{O^0} + n_{O^-}$).

The task of the calculation of the anion distribution was thereby subdivided into two parts. First, the probability of the formation (relative concentration) of silicon tetrahedrons with 0, 1, 2, 3, and 4 bridging bonds was calculated (they were later named Q^n species, see below)

$$X_{Q^n} = P_n = \frac{4!}{n!(4-n)!} p^{4-n} (1-p)^n, \quad (21)$$

where $0 \leq n \leq 4$ is the number of the bridging bonds. Such a Bernoulli distribution is based on the assumption of the equal ability of end-positioned bonds in Q monomers to participate in polycondensation reactions. This approximation follows from the assumption that the equilibrium constant of reaction (3) is independent of the type of the Q species participating in the formation of chain and ring structures (5), (6). In fact, this assumption is equivalent to the principle of equal reaction ability of nonbridging oxygen atoms. Thus, Q^n structural units are considered to be "building blocks" of real anion complexes, whose probability of formation (relative concentration) was calculated using the P_n values (21) computed by a specialized algorithm and with regard for the isomerization of the possible polymers [25].

The concentrations of polyanions (including isomers) were calculated by statistical methods. In this model, the probability of the occurrence of species Q^0 (the fraction of the SiO_4^{4-} monomer among all Si atoms) coincides with P_0 and is equal to p^4 . The probability of the formation of the $Si_2O_7^{6-}$ dimer is determined as the product of the probability P_1 by the value of $P_1 / (1 - P_0)$, which is the fraction of Q^1 species among all species with bridging bonds. Applying an analogous logic, Lacy [25] derived analytical expressions and calculated the probabilities of the formation of 300 isomers for anion groups with no more than eight Si atoms ($1 \leq i \leq 8$, Table 1). However, he failed to determine the MMD of a silicate melt in the general form [25] because of the practical impossibility of the analytical description of the complete spectrum of isomer species for polyanions with $i \geq 9$ and the absence of suitable computer equipment. Nevertheless, the approach underlain by the use of Q^n structural units as the basis for simulating anion distributions seems to be construc-

tive. It is thereby important that the distribution of Q^n species in a silicate melt can be evaluated from experimental results [38, 39, 40, 64] or calculated theoretically with the use of empirical equilibrium constants of polycondensation reaction (3) [26, 27].

Distribution of Q^n structons and the significance of the Toop-Samis model. The term structon was proposed to denote the minimum set of structural units sufficient to compose polymer complexes of various sizes [65]. Fraser [26, 27] extended this concept over silicon-oxygen tetrahedrons with different proportions of end-positioned O^- and bridging O^0 atoms and utilized proportions of Q^n quasispecies (Q^n structons) in the thermodynamic description of the mixing properties of silicate liquids.¹ Like in [25], he proposed to calculate the relative concentrations of the five main structural units by combinatorial expressions following from (20), (21)

$$X_Q^0 = P_0 = p^4, \quad X_Q^1 = P_1 = 4p^3(1-p),$$

$$X_Q^2 = P_2 = 6p^2(1-p)^2, \quad X_Q^3 = P_3 = 4p(1-p)^3, \quad (22)$$

$$X_Q^4 = P_4 = (1-p)^4,$$

in which all four Si-O bonds of the Q^4 quasispecies are bridging, and the ratio of bridging to nonbridging bonds in the Q^3 , Q^2 , and Q^1 structons are 3 : 1, 1 : 1, and 1 : 3, respectively. Quasispecies Q^0 containing four end-positioned O^- atoms is the only structon of this group coinciding with an anion actually present in the polymerized matrix: the SiO_4^{4-} monomer.

As can be easily seen in (22), the expected distribution of Q^n structons as a function of p is symmetrical (Fig. 1), thus highlighting the absence of an explicit dependence on temperature or the composition of the system. The proportions of quasispecies are determined exclusively by the proportions of nonbridging and bridging bonds, according to (20). The functional characteristics of this ideal (stochastic) distribution of Q^n structons (Fig. 1) and the chemical composition of silicate systems can be estimated by the method [22], see formulations in [26, 27] for binary MeO-SiO₂ systems. In application to alkaline silicate and combined MeO-Me₂O-SiO₂ systems, this approach implies the solution of systems of equations including the balance of bridging and nonbridging bonds in Si-O tetrahedral

$$4n_{SiO_2} = 2n_{O^0} + n_{O^-}, \quad (23)$$

with the electrical neutrality of the system expressed as

$$2n_{Me^{2+}} + n_{Me^+} = 2n_{O^{2-}} + n_{O^-}, \quad (24)$$

¹ Note that structons are understood in [46, 54] as a certain set of anion species necessary to realize the thermodynamic model of melt proposed by the authors. We will apply this term in its traditional formulation [25, 26, 27] and use the term *Si anions* when speaking about polymer complexes (17)–(18).

where $n_{\text{SiO}_2} + n_{\text{Me}^{2+}} + n_{\text{Me}^+} = 1$ (in recalculation into 1 mole of the initial melt), and the expression for the equilibrium constant of polycondensation reaction (3)

$$K_e^{\text{TS}} = x_{\text{O}^0} x_{\text{O}^{2-}} / (x_{\text{O}^-})^2 = n_{\text{O}^0} n_{\text{O}^{2-}} / (n_{\text{O}^-})^2. \quad (25)$$

Solving the system of equations (23)–(25), one can evaluate the concentration of oxygen quasispecies n_{O^0} , n_{O^-} , and $n_{\text{O}^{2-}}$ in a binary and ternary silicate system with various doubly and triply charged cations. The calculated values of n_{O^0} and n_{O^-} are substituted into (20), and this makes it possible to use (21), (22) to estimate the proportions of Q^n structons. Thereby the effects of the silicity of the melt are taken into account via (23), and the effect of the type (list) of cations is implicitly accounted for through differences between K_e^{TS} values for various metals. As a result, the dependence of the equilibrium constant K_e^{TS} (25) on temperature and composition determines the distribution of Q^n structons as an implicit function of these parameters.

Problem of the calibration and application of polycondensation constants. The development of generalized models for polymer equilibria combining the advantages of the chemical approach (5), (6) and the relative simplicity of the Toop–Samis quasichemical model (3), (23)–(25) depends on the possibility of calibration of the equilibrium constants K_e^{TS} for various oxides. Polycondensation constants (25) are evaluated by optimizing experimental data on the activity of MeO and Me_2O in silicate melts of various compositions. The main criterion of the consistency of the theory and experiment is the compatibility of the calculated mole fractions of O^{2-} with the established dependences of the activity of oxides or the mixing entropy of melt components on its composition. This method was applied to derive the first estimates of K_e^{TS} for binary MeO–SiO_2 systems with Fe, Mn, Ca, Pb, and Zn oxides [24]. A more comprehensive review of polycondensation constants (with regard for alkali oxides) was given in [46]. Some difficulties are encountered when these values are extrapolated to multicomponent systems because of the necessity for the calculation of an “integral” (weighted average) value of K_e^{TS} in a cation matrix of complex composition. The solution of this problem was considered in [44, 46, 47], in which a semiempirical method was proposed for the calculation of these constants for multicomponent systems

$$K_e^{\text{TS}} = \exp[4.622(\sum x_{\text{Me}} \gamma_{\text{Me}} + \sum x_{\text{T}} \gamma_{\text{T}}) - 1.1445], \quad (26)$$

where the fractions of metal cations (x_{Me}) and tetrahedrally coordinated ions (Si^{4+} , Al^{3+} , referred to as x_{T}) are multiplied by the tabulated values for the *basicity moderating parameter* γ_{Me} and γ_{T} for each cation. The basic

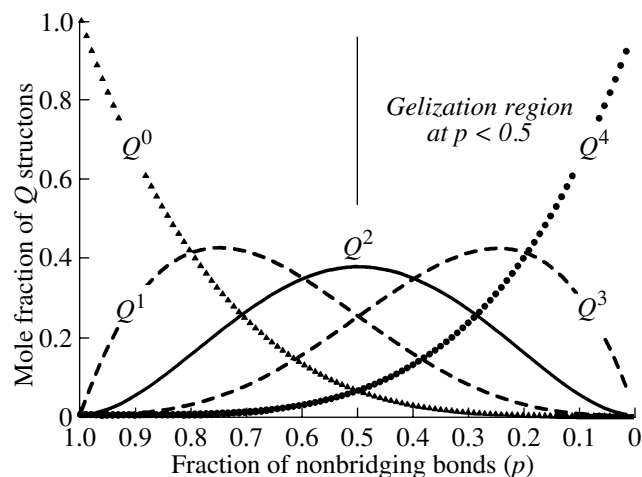


Fig. 1. Statistically expected distribution of Q^n structons depending on the fraction of nonbridging oxygen bonds p (20) in the polymerized silicon–oxygen matrix.

Calculated by Eq. (22) in the approximation of the equal reaction ability of nonbridging bonds. The gelization region of the silicate matrix and the development of infinitely large three-dimension “ring” complexes correspond to $p < 0.5$.

information is thereby the values of K_e^{TS} quantified for binary systems. It is hard to assay the consistency of this approach, particularly considering the fact that expression (26) disregards the temperature effect. However, the efficiency of this approach was proved by the successful description of the Fe oxidation state and S speciation in natural silicate melts [44, 48].

The theoretical approaches discussed above and available empirical information on the equilibrium constants of polycondensation reactions (3), (25), (26) make it possible to relate the activity of free oxygen ions and the degree of polymerization of the silicate matrix (16), (20). This provides the basis for calculating the distribution of Q^n structons in “ternary” $\text{MeO–Me}_2\text{O–SiO}_2$ systems depending on the melt composition (21), (22). This, in turn, makes it possible to modify the approach [25] for the solution of the statistical problem of the evaluation of the mass molecular distributions with regard for the probability of the formation of various polymer complexes. The technique of the solution of this problem in the approximation of the equal reaction ability of nonbridging bonds in Si–O tetrahedrons was justified in [55] and is briefly described below.

MONTE CARLO MODELING OF MMD

In the approach proposed here, a polymer complex of any composition $((\text{Si}_i\text{O}_{3i+1-j})^{2(i+1-j)-})$ (2) is regarded as an ensemble of various Q^n structons. If the general distribution of Q^n structons in the system is specified, then the polymerized silicate matrix can be modeled as an ensemble of various anions, i.e., diverse successions

of Si–O tetrahedrons with various proportions of non-bridging and bridging bonds. The concentration of the O^{2-} ion is determined by the distribution function of Q^n structons and is independent of the processes forming polymer complexes on their basis. This makes it possible to disregard the presence of free oxygen ions and model the structure of the polycondensated system as a result of successive interactions of Q^n species.

Here we assume that the distribution of Q^n structons is specified by the Bernoulli formula (20)–(22)². Thereby one Si–O⁰–Si bond is formed by reaction (3) at each modeling step as a result of interaction of structons. Obviously, the polymerization of the Q^1 species can form only one bridging bond. This “potentially bridging” bond will be referred to as saturated. The Q^2 , Q^3 , and Q^4 structons have two, three, and four unsaturated bonds, respectively. According to the definition formulated above, the polymerization of silicate melt is a process of saturation (realization) of unsaturated bonds. Hence, the formation of an ensemble of polymerized anions in melt can be modeled as the successive accumulation of polymers composed of structons with unsaturated bridging bonds. The only species that forms no bridging bonds is Q^0 , which is interpreted as the SiO_4^{4-} ion and is added to the modeled ensemble of polyanions as an individual structural unit.

Modeling algorithm for the polycondensation of silicate melt. Consider N initial “monomers,” which are Q^n species distributed according to formula (22). Let us randomly select a succession of their participation in polymerization reactions. With a probability P_0 , the first species to participate in them may be Q^0 . If the first randomly selected monomer is Q^0 , then number of the SiO_4^{4-} species in the silicate melt is equal to 1. After that, at each selection of the Q^0 species, the number of the SiO_4^{4-} ions increases by one. If the first randomly selected monomer is the structon Q^1 (the probability of this event is P_1), then this potential polymer species is unsaturated, and the selection of the monomer succession will be continued. Evidently, the saturation of the bond of the structon Q^1 selected at the first step will continue only after the selection of a species having unsaturated bonds. The probability of this event is equal to $(1 - P_0)$, because the participation of monomer Q^0 in the reactions cannot result in the saturation of bridging bonds, and the removal of this monomer from the reaction is associated with an increase in the number of SiO_4^{4-} ions in the silicate melt. Consequently, the

next monomer in the developing succession may be Q^1 . The probability of this event for the second monomer in the succession of reactants is $P_1/(1 - P_0)$. In this situation, the unsaturated bridging bonds of two Q^1 structons are realized in the form of one saturated bond of the $Si_2O_7^{6-}$ dimer, which is a completed polymer chain and is added to the ensemble of species of the modeled melt.

The probability of this event is equal to $P_1^2/(1 - P_0)$ and coincides with that in Lacy’s (1965) method. After a saturated dimer (or any other saturated polymer species) is formed, the development of another polymerization succession is initiated. If the second species to participate in the polymerization succession is Q^2 , Q^3 , or Q^4 , then the dimer resulting from the formation of a single bridging bond will not be saturated (one, two, or three unsaturated bonds remain), and the process forming polymer will continue. However, if the second polymer in this succession is the Q^2 structon and the third monomer will be Q^1 , then the trimer thus produced will have no unsaturated bonds and should be interpreted as the $Si_3O_{10}^{8-}$ ion. The probability of formation of this ion is equal to $P_1^2 P_2/(1 - P_0)^2$.

The formation of polymers in this model is limited by an important constraint: two monomers in a single succession can be connected only through one bridging bond. This constraint is equivalent to the impossibility of “connecting” silicate tetrahedrons via an edge or face, because the tetrahedrons can share only apexes. This precludes, for example, the formation of cyclic dimers composed of Q^1 and Q^2 ($Si_2O_6^{4-}$) or two Q^2 ($Si_2O_5^{2-}$) species. Analogously, other metastable “ring” structures, such as $Si_3O_8^{4-}$, and the $Si_4O_{10}^{4-}$ tetramer are excluded (Table 1). The minimal cyclic polymer that can be produced in this situation is the $Si_3O_9^{6-}$ ion, which is made up of three Q^2 structons. The probability of formation of this trimer is made up in our model of two events: (1) the formation of the saturated trimer consisting of three Q^2 species and having two unsaturated bonds and (2) subsequent cyclization via the formation of a bridging bond between the first and third unsaturated monomers in the trimer. Evidently, the probability of the former event is equal to $P_2^3/(1 - P_0)^2$. The further fate of the unsaturated trimer in our model may be as follows: (1) either the connection with any of the unsaturated Q^n species (which remain in the reservoir of the possible reactants) or (2) cyclization, i.e., the formation of a bridging bond between the first and third monomers.

If the next monomer in our succession is Q^1 , i.e., a species with one unsaturated bond, it can be connected with an unsaturated trimer in two ways, according to the number of unsaturated bonds of this trimer, and

² The utilization of the Bernoulli distribution, i.e., the assumption of the principle of equal reaction ability, is not necessary for the application of this approach, because the proposed algorithm and modeling technique are independent of the distribution of Q^n species [55]. Our oncoming papers will present calculations with the distributions of structons that were experimentally measured by Raman and NMR spectroscopic methods.

cyclization can proceed in only one manner (see above). Under the assumption of the equal reaction ability of unsaturated bonds, the probability of cyclization in the case of Q^1 is equal to 1/3. In the case of Q^2 , this probability is equal to 1/5, because two unsaturated bonds of this structon have four possibilities of forming a bridging bond with two unsaturated bonds in the trimer. In the general case, if the unsaturated polymer has m unsaturated bonds that can form k permitted bridging bonds, the probability of the formation of a cyclic bond is

$$P_c = \frac{\frac{k}{m+k}P_1 + \frac{k}{2m+k}P_2 + \frac{k}{3m+k}P_3 + \frac{k}{4m+k}P_4}{1 - P_0} \quad (27)$$

$$< \frac{k}{m+k},$$

where P_c is the probability of cyclization. The more systematic evaluation of the probability of formation of a cyclic polymer (27) makes our probabilistic model different from that in [25].

The proposed statistical model is thus reduced to the random links of bridging bonds of various Q^n structons with the formation of polymer chains or cyclic complexes. Each polymer succession develops until the complete saturation of the bridging bonds of the newly formed structure. The constraint imposed onto this process is the connection of structon pairs by only one bridging bond. For a polymer succession including unsaturated monomers, the probability of self-cyclization is determined by Eq. (27), and the probability of the continuation of the succession of Q^n species (an increase in the size of the polymer) is rendered by the formula

$$P_{Q^n} = \frac{nm}{nm+k}P_n, \quad (28)$$

where P_{Q^n} is the probability of the continuation of the succession with monomer Q^n , and P_n is the fraction of Q^n structons in system (20)–(22).

Computer implementation of the model. In order to conduct calculations on the basis of the proposed stochastic model, our earlier STRUCTON software program package [55] was supplemented with a routine for the calculation of the initial distribution of Q^n structons by formulas (20)–(22). An MMD is modeled by this program with a random-number generator (RNG) that evenly covers the range of the number axis from 0 to 1. RNG simulates discrete random value ξ , which assumes values ξ_{n+1} ($n+1 = 1, 2, \dots, 5$ according to the number of structons Q^n) with probabilities p_1, p_2, \dots, p_5 . For this purpose, the whole [0, 1] interval is subdivided into five segments, all of which having lengths p_{n+1} . RNG yields a number between 0 and 1. Depending on the segment into which the value falls, the random value acquires a value ξ_{n+1} . This simple procedure pro-

vides the basis for the application of a method that is a variant of the Monte Carlo technique.

The beginning of simulations by the STRUCTON program involves specifying (or evaluating, see below) the value of p , which characterizes the fraction of “non-bridging” oxygen bonds (20), and determining the distribution of Q^n structons by formulas (22). The determined probabilities P_n were utilized to realize the random value of the outcome of Q^n species (Fig. 2). If the first structon turned out to be Q^0 , then the number of SiO_4^{4-} ions in the modeled melt was increased by one. If an unsaturated species Q^n appeared, then the number of unsaturated bonds in the polymer chain was calculated, and the random value was generated, which assumed one of the two values corresponding to cyclization or the addition of another Q^n monomer. The corresponding probabilities are equal to $k/(nm+k)$ for the formation of a cycle and $nm/(nm+k)$ for an increase in the size of the polymer complex. During the next stage, it was “determined” which pairs of unsaturated bonds are cyclized in the polymer or with which of the unsaturated bonds another Q^n species was linked based on the principle of equal reaction ability. Upon the saturation of all bonds in the structon succession, i.e., when a given polyanion is completely formed, its composition (2), size, and charge were written into a file. Correspondingly, the number of polymer species was increased $N_p = N_p + 1$, and the number of Q^n structons in the initial reservoir was decreased by one $N = N - 1$. The simulation of polymerization of a silicate matrix was terminated when current value $N = 0$.

The simulation sequence presented above (Fig. 2) characterizes one model calculation at $p = \text{const}$. With regard for the probabilistic character of the model, such calculations should be carried out a few dozen times with the evaluation of the reproducibility and statistical parameters of the calculated distributions at the same starting conditions. For specified p values (20), we conducted 50 such realizations. Taking into account that each calculation involves $N = 10000$ initial monomers Q^n , the output of MMD modeling at a constant proportion of bridging and nonbridging bonds can be regarded as a result of calculations for 0.5×10^6 Q^n structons.

MODELING RESULTS

The molecular-mass distributions were calculated for the interval $0.52 \leq p \leq 98$ (20) with a step $\Delta p = 0.02$. Thus, in the course of $24 \times 50 = 1200$ simulations, we modeled a broad spectrum of the states of the polymerized matrix, from the predominance of the SiO_4^{4-} monomer with a minor amount of the $\text{Si}_2\text{O}_7^{6-}$ ion almost to the gelization point at $p = 0.50$ (Fig. 1), at which hundreds of Si–O species are present and the anion complexes unrestrictedly increase. Table 2 and Fig. 3, which are based on the results of the calculations

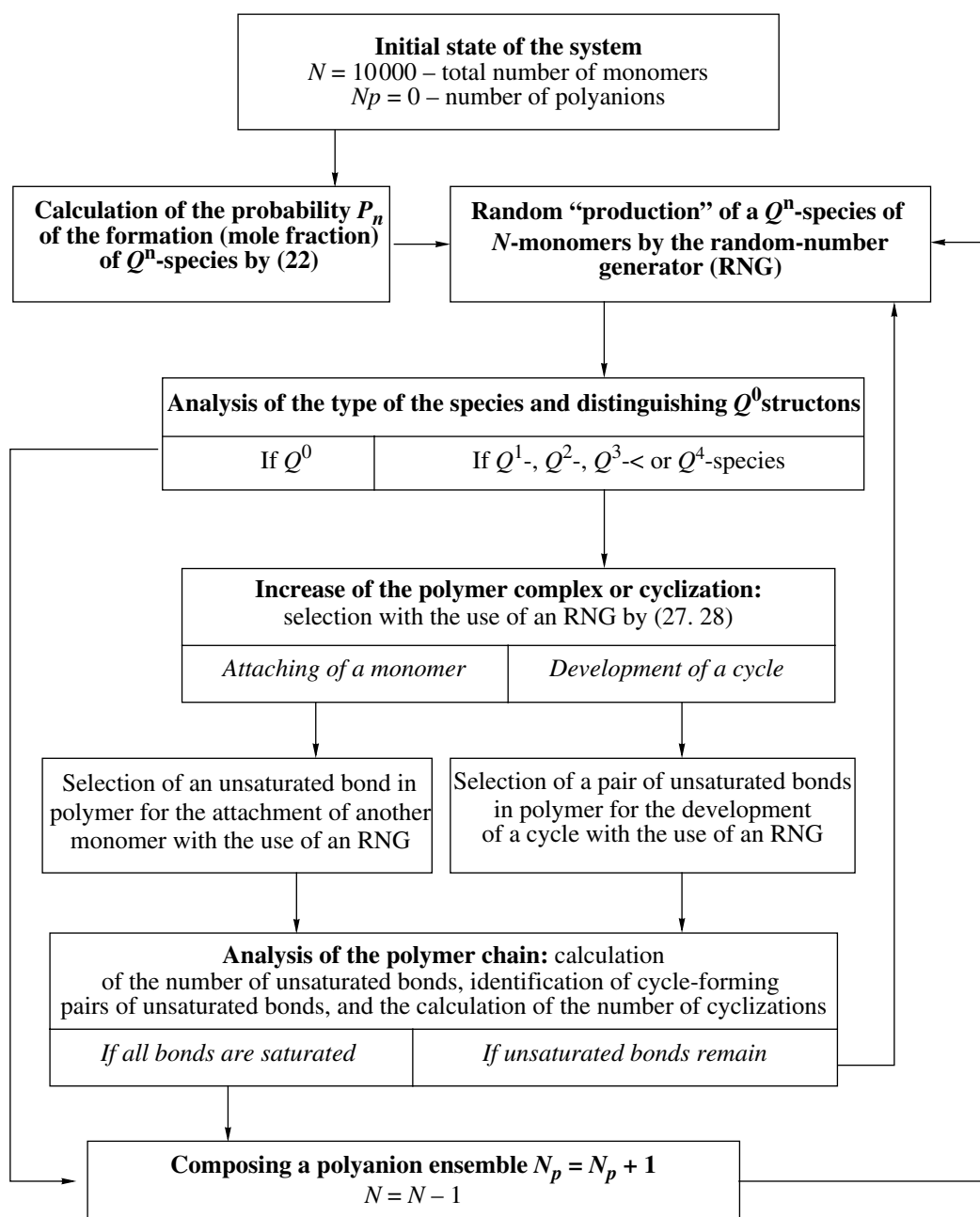


Fig. 2. Control-flow diagram of the STRUCTON software program package developed to simulate molecular-mass distributions of polyanions on the basis of the distribution of Q^n structons in silicate melt [55].

at $p = 0.60$, illustrate the diversity and reproducibility of the modeled ensembles and the relative concentrations of the polyanions. These calculations model a moderate degree of polymerization of the system $\alpha = 1 - p = 0.4$ (16), in which $\sim 13\%$ of the original Q^n structons is the SiO_4^{4-} ion, and the rest are grouped in complexes and form, together with the SiO_4^{4-} monomer, 2658 ± 40 species on average from each 10000 original monomers. Hence, the average mole fraction of the SiO_4^{4-} ion among the polyspecies is close to 0.5 ($\sim 0.13 \times 10000/2658$), and

the other linear and “ring” structures display a decrease in the concentration with increasing size of polyanions i and the cyclization number j . It is worth noting that this decrease is monotonous for linear structures ($j = 0$) but shows maxima on the distribution lines for ring complexes ($j \geq 1$).

Our MMD simulations testify that the stability of the solution of the problem for a given number of original Q monomers depends on the fraction of polymerized species. At concentrations lower than 0.1% (as is typical of species with the number of cyclized bonds

$j \geq 3$), the number of ring complexes shows “peak” distributions (Fig. 3). A measure of the “stability” of the modeled ensembles may be the dispersion of the polymer concentrations expressed as the standard deviation (1σ) evaluated for each type of the species from the results of 50 calculations and normalized to the corresponding mole fraction (Table 2). The table lists 166 linear and ring structures, whose appearance in this calculation series was detected at least four times. For the predominant low-molecular species ($i \leq 8, j \leq 1$), the standard deviations of the calculated values do not exceed 20%. High-molecular complexes with $8 \leq i \leq 20$ show reproducibility within 100–300%, but this pertains to species whose concentrations are no higher than 0.01–0.1 mol %. Note that the 166 species and single complexes with $41 \leq i \leq 93$ (Table 2) comprise the whole diversity of the polymers obtained in our simulations for 500000 species. It can never be realized in practical calculations of a single polymerization succession for $N = 10000$. The average number of polymer types obtained in 50 simulations at $p = 0.60$ is 92.2 ± 4.4 .

Another important observation, which follows from the analysis of the structure of data from Table 2, pertains to the finiteness of the anion ensemble. This is manifested in the limited length of the chains ($i \leq 25$) and the size of the ring complexes, which are reduced polymer successions that shorten with progress in cyclization j . It was mentioned above that the main reason for the limited maximum size of the chain anions is the self-cyclization of end-positioned oxygen atoms, whereas the factor “hampering” cyclization (particularly for small species) is caused by the “prohibited” sharing of edges and faces of Si–O tetrahedrons. Figure 4 displays a systematic increase in the average number of Si–O complexes of various types and a decrease in the overall number of polyspecies in the system as p is changed from 0.98 to 0.52. These results are obviously different from those in [25]. The assessment of the potential set of the polyanions by the STRUCTON program package implicitly allows the presence of isomer complexes [through the calculation of the average concentrations of polymers of certain composition (2), regardless of their geometry (set of Q^n structons)]. Lacy’s [25] results provide an estimate for the probable concentration of each type of species of the same composition but different configuration in relation to the loci where bridging bonds are formed in the polymer “chain.” Because of this, our calculations never yield more than four types of species including eight Si atoms ($i = 8$), whereas more than 160 structural units was proposed for similar compositions in [25].

The deliberate limitation of the “configurational constituent” in our model is not of principal character and does not effect the calculation of the overall number of anions (12) and the concentrations of the predominant small-sized species (Fig. 3). Moreover, it seems to be convenient for the further analysis of the results of the statistical simulations to even more “reduce” the obtained information using Esin’s method

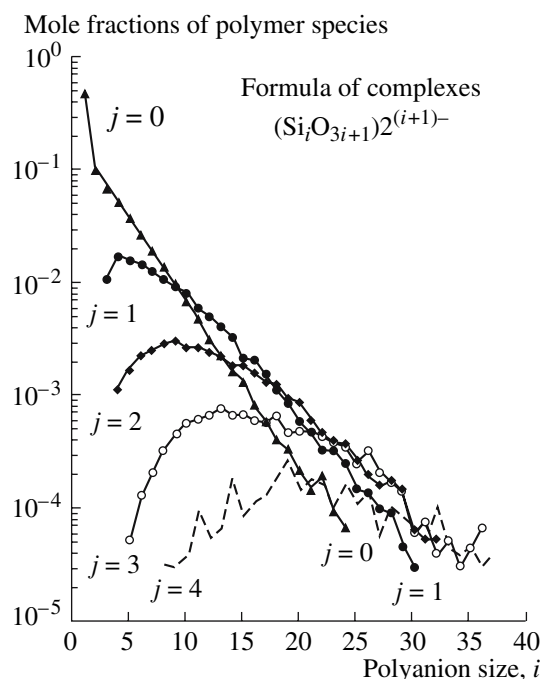


Fig. 3. Molecular-mass distribution of chain ($j = 0$) and “ring” ($1 \leq j \leq 4$) complexes, calculated by the STRUCTON software program package according to the results of 50 simulations at $p = 0.60$.

The mole fractions and their dispersions are reported in Table 2. The complete anion ensemble includes 2658 ± 40 polymerized species on average (of 10000 initial Q^n structons), which represent approximately 200 various complexes having a size of $1 \leq i \leq 93$. The presence of isomers is implicitly taken into account as the calculation result of the average concentration of polymers of certain composition (2) regardless of their geometry.

[20, 34]. This approach involves the summation of polyanion concentrations in a succession corresponding to the same degree of cyclization j (see columns in Table 2). This makes it easier to compare the calculation results for different p values or complementary degree of polymerization α (Table 3). Figure 5a shows the distributions of the four predominant polyspecies (the SiO_4^{4-} monomer, $\text{Si}_2\text{O}_7^{6-}$ dimer, $\text{Si}_3\text{O}_{10}^{8-}$ linear trimer, and $\text{Si}_3\text{O}_9^{6-}$ ring trimer), whose aggregate concentrations vary from 99.99% at $p = 0.98$ to 62.52% at $p = 0.52$. Figure 5b characterizes the integral distributions and presents data (along those for SiO_4^{4-}) on the relative proportions of the whole set of the chain anions ($i > 1$), singly cyclized ring structures ($j = 1$), and three-dimension complexes ($j \geq 2$) corresponding to general formula (2).

In the case of the monomer, the concentrations systematically decrease within the range of $0.98 \leq p \leq 0.58$, and the mole fraction of the SiO_4^{4-} ion increases at a further increase in the degree of polymerization of the system. This causes the fast decrease in the overall

Table 2. Mole fractions and dispersions of concentrations of polyanions for chain ($j = 0$) and ring ($j \geq 1$) complexes calculated based on the results of 50 simulations for $p = 0.60$

Anion size, i	Number of closures (cyclizations) of intramolecular bonds, j						
	$j = 0 (\times 10^{-2})$	$j = 1 (\times 10^{-2})$	$j = 2 (\times 10^{-3})$	$j = 3 (\times 10^{-4})$	$j = 4 (\times 10^{-4})$	$j = 5 (\times 10^{-5})$	$j = 6 (\times 10^{-5})$
1	48.54 (1.5)	–	–	–	–	–	–
2	9.71 (5.8)	–	–	–	–	–	–
3	6.60 (7.7)	1.05 (14)	–	–	–	–	–
4	5.00 (8.6)	1.64 (15)	1.13 (56)	–	–	–	–
5	3.60 (9.7)	1.53 (14)	1.69 (45)	0.52 (247)	–	–	–
6	2.60 (12)	1.41 (14)	2.22 (41)	1.28 (200)	–	–	–
7	1.86 (15)	1.23 (19)	2.49 (31)	2.02 (124)	–	–	–
8	1.33 (16)	1.03 (18)	2.81 (33)	3.23 (98)	3.1 (339)	–	–
9	0.955 (20)	0.894 (19)	2.96 (41)	4.43 (74)	3.0 (339)	–	–
10	0.666 (24)	0.762 (24)	2.63 (36)	5.58 (97)	3.8 (300)	–	–
11	0.468 (33)	0.580 (23)	2.63 (30)	6.07 (88)	9.8 (185)	–	–
12	0.308 (33)	0.483 (25)	2.37 (38)	6.63 (65)	5.3 (286)	–	–
13	0.229 (37)	0.398 (23)	2.13 (41)	7.59 (60)	6.0 (229)	–	–
14	0.165 (49)	0.314 (34)	1.77 (37)	6.63 (77)	19.5 (134)	–	–
15	0.131 (47)	0.214 (46)	1.80 (51)	6.69 (64)	8.3 (208)	–	–
16	0.082 (58)	0.202 (42)	1.54 (53)	5.95 (62)	11.2 (152)	3.1 (339)	–
17	0.058 (89)	0.151 (52)	1.27 (59)	5.87 (57)	12.8 (151)	–	–
18	0.040 (106)	0.111 (50)	1.22 (53)	6.46 (72)	17.4 (146)	3.8 (300)	–
19	0.033 (115)	0.082 (62)	0.935 (56)	4.59 (89)	26.3 (103)	–	–
20	0.021 (130)	0.057 (75)	0.858 (81)	4.75 (82)	14.4 (166)	5.2 (247)	–
21	0.014 (138)	0.047 (88)	0.588 (96)	4.60 (79)	18.0 (181)	6.0 (260)	–
22	0.019 (128)	0.032 (111)	0.452 (79)	4.21 (86)	16.5 (158)	5.3 (247)	–
23	0.009 (197)	0.032 (129)	0.368 (102)	3.77 (113)	9.8 (185)	3.8 (300)	–
24	0.007 (265)	0.024 (123)	0.376 (85)	3.39 (102)	16.5 (164)	4.6 (270)	–
25	0.003 (339)	0.014 (156)	0.263 (128)	2.41 (128)	10.5 (202)	6.0 (261)	–
26	–	0.013 (182)	0.196 (139)	3.24 (114)	15.0 (149)	–	–
27	–	0.009 (199)	0.157 (135)	2.03 (148)	5.40 (247)	6.7 (300)	–
28	–	0.009 (196)	0.173 (131)	1.66 (137)	10.5 (175)	3.0 (339)	–
29	–	0.004 (270)	0.144 (174)	1.36 (174)	8.3 (188)	–	–
30	–	0.003 (339)	0.068 (240)	0.60 (229)	6.8 (213)	4.5 (270)	–
31	–	0.004 (270)	0.053 (348)	0.76 (200)	5.3 (352)	3.7 (300)	–
32	–	–	0.053 (247)	0.38 (300)	10.5 (160)	5.2 (247)	–
33	–	–	0.053 (284)	0.52 (285)	4.5 (270)	6.0 (229)	–
34	–	–	0.053 (247)	0.30 (339)	3.8 (300)	–	3.8 (300)
35	–	–	–	0.45 (270)	4.5 (270)	3.0 (339)	3.0 (339)
36	–	–	–	0.67 (240)	3.0 (339)	–	–
37	–	–	–	0.38 (300)	3.7 (300)	–	–
38	–	–	–	–	–	–	–
39	–	–	–	–	3.1 (339)	–	–
40	–	–	–	–	3.7 (300)	–	–

Note: dispersion is the standard deviation (1σ) expressed in % of the mole concentration. The table reports 166 complexes whose appearance in a series of 50 simulations was noted at least four times. Single (usually one or two) complexes of size $41 \leq i \leq 93$ amount to no more than 0.04% of the average amount of polymerized species (2658 ± 40).

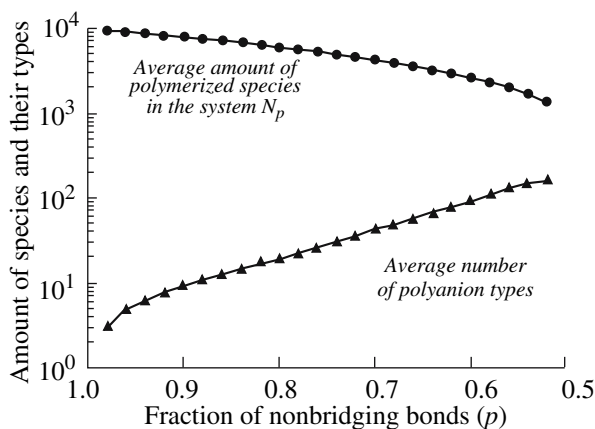


Fig. 4. Dependence of the average number of silicon–oxygen compositions of various types and the overall amount of polyanions on the relative fraction of nonbridging oxygen bonds p (20) in the silicate matrix.

Calculated by the STRUCTON software program package. Averaging at specified $p = \text{const}$ was conducted based on the results of 50 simulations for 10000 original Q^n species. The reported errors correspond to the $\pm 1\sigma$ interval.

number of polymer species because of an increase in their size (see Table 3). An increase in the concentrations of small species (including the O^{2-} ion, see below) relative to high-molecular complexes is a distinctive feature of ion–polymer models [13, 20]. The distribution of the total concentration of linear polymers ($j = 0$) and ring complexes of various types exhibits relative maxima (Fig. 5b), whose mode p_j shifts with decreasing p : $p_0 \geq p_1 \geq p_2 \dots \geq p_j$ (where J is the maximum possible number of cyclizations of nonbridging O^- bonds at a given degree of polymerization). Note that, in spite of a decrease in the concentration of complexes of certain type, the fraction of small species of this cluster may increase, as took place for the $\text{Si}_2\text{O}_7^{6-}$ ion (Fig. 5a) in the general massif of chain polymers (Fig. 5b).

Evaluation of the concentrations of the O^{2-} ion.

The solution of the problem of MMD modeling for Si anions in a polymerized silicate matrix makes it possible to calculate the fraction of the O^{2-} ion (8b) with respect to the total amount of anions (12) in $\text{MeO–Me}_2\text{O–SiO}_2$ systems of given composition. This problem can be solved as follows.

(I) First, the number of virtual atoms (n_{O^0} , and n_{O^-}) and ions of free oxygen are calculated for 1 mole of melt at given K_e^{TS} values by Eqs. (23)–(25) (examples of these estimates for $K_e^{\text{TS}} = 0.001$ and 0.1 are shown in Fig. 6). Using n_{O^0} and n_{O^-} and Eq. (20), the weighted mean fraction of nonbridging oxygen bonds p in the silicate matrix is calculated.

(II) Then MMD is modeled for a given p and the amount of polymerized species in the system $\Sigma\text{Si-anions}$

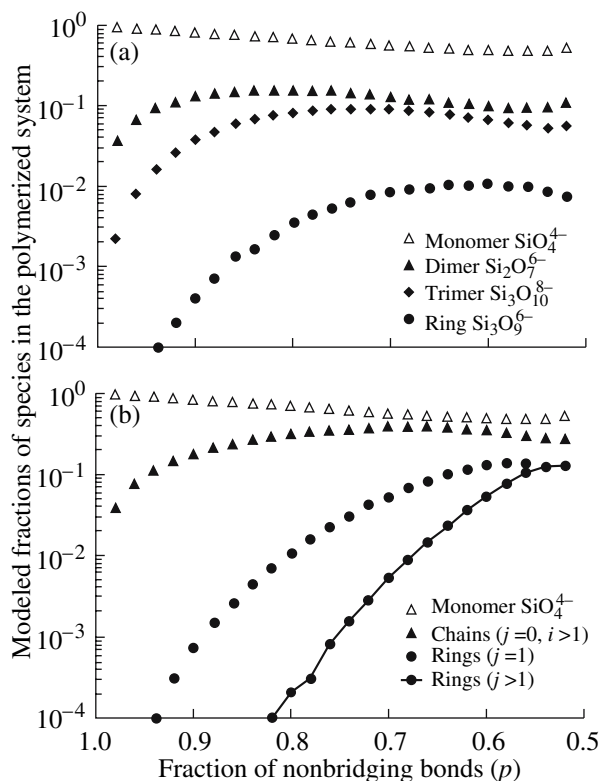


Fig. 5. Distribution characteristics of the predominant types of polyspecies and the concentration of the sum of chain anions and ring complexes depending on the relative fraction of nonbridging oxygen bonds p (20).

(a) Individual anions, (b) SiO_4^{4-} monomer in comparison with the overall concentration of ring structures ($i \geq 2$), singly cyclized “ring” ($j = 1$), and three-dimension complexes ($j \geq 2$). The results of species summation in successions $j = \text{const}$ correspond to the formula of polyanions in reaction (2).

is calculated (12). For this Bernoulli distribution of Q^n structons, such estimates can be obtained using approximations for the average amount of polymers N_p among 10000 modeled species: $N_p = f(p) \rightarrow X_p = 10^{-4}N_p \rightarrow \Sigma\text{Si-anions} = X_p N_{\text{Si}}$, where N_{Si} is the amount of Si atoms in one mole of the original melt, and $f(p)$ is a derivative function selected for the description of the established dependence of N_p on p (Fig. 4). It is, however, more convenient in practice to conduct calculations with another important parameter, characterizing the average size of the Si-anion, i_{av} . This parameter is calculated from the results of modeling by the STRUCTON program at each p value (Table 3), and its dependence on the fraction of nonbridging bonds is accurately enough approximated by a sixth-degree polynomial (Fig. 7). Because, by definition, the value of i_{av} is the weighted mean (with regard for mole fractions) size of polymers,

$$\Sigma\text{Si-anions} = N_{\text{Si}}/i_{\text{av}}. \quad (29)$$

Table 3. Comparison of MMD modeling at $p = 0.54$ and $p = 0.60$

For nonbridging bonds $p = 0.54$					For nonbridging bonds $p = 0.60$				
Species	Number	X (mol)	Av. charge	Av. siz	Species	Number	X (mol)	Av. charge	Av. siz
SiO ₄	841	0.47541	-4.0	1.00	SiO ₄	1250	0.47295	-4.0	1.000
<i>Chains</i>					<i>Chains</i>				
Si ₂ O ₇	175	0.09893	-	-	Si ₂ O ₇	262	0.09913	-	-
Si ₃ O ₁₀	106	0.05992	-	-	Si ₃ O ₁₀	203	0.07681	-	-
Total	503	0.28434	-10.6	4.27	Total	906	0.34279	-10.8	4.40
<i>Rings</i>					<i>Rings</i>				
Si ₃ O ₉	16	0.00904	-	-	Si ₃ O ₉	32	0.01211	-	-
J = 1	215	0.12154	-18.0	9.01	J = 1	357	0.13507	-16.1	8.04
J = 2	99	0.05596	-24.4	13.20	J = 2	84	0.03178	-22.0	12.01
J = 3	45	0.02544	-35.4	19.69	J = 3	35	0.01324	-30.6	17.31
J = 4	27	0.01526	-59.8	32.89	J = 4	7	0.00265	-40.6	23.29
J = 5	8	0.00452	-55.3	31.63	J = 5	2	0.00076	-34.0	21.00
J = 6	8	0.00452	-72.8	41.38	J = 6	1	0.00038	-58.0	34.00
J = 7	7	0.00396	-59.1	35.57	J = 7	1	0.00038	-72.0	42.00
J = 8	5	0.00283	-94.4	54.20	J = 8	-	-	-	-
J = 9	5	0.00283	-118.4	67.20	J = 9	-	-	-	-
J = 10	1	0.00057	-176.0	97.00	J = 10	-	-	-	-
J = 11	-	-	-	-	J = 11	-	-	-	-
J = 12	3	0.00170	-172.7	97.33	J = 12	-	-	-	-
J = 13	-	-	-	-	J = 13	-	-	-	-
J = 14	2	0.00113	-137.0	81.50	J = 14	-	-	-	-
Total	1769	1.00000	-12.2	5.65	Total	2643	1.00000	-9.1	3.78

Note: in the calculations at $p = 0.54$, the appearance of six species of average size i about 97 and 87, a number of cyclization j from 10 to 14, testifies that the gelization point is approached, at which an unlimited increase in the polymerization successions takes place.

(III). The values of N_{Si}/i_{av} and $n_{O^{2-}}$ are substituted into (12) and are utilized to calculate the concentration of the free oxygen ion O^{2-} in system (8b)

$$x_{O^{2-}} = n_{O^{2-}} / (n_{O^{2-}} + N_{Si}/i_{av}). \quad (30)$$

In Fig. 8, the compositional dependences of the concentration of the free oxygen ion O^{2-} calculated for MeO-SiO₂ systems in the quasichemical model approximation ($[O^{2-}]$, see [24]) are compared with calculations by (30) with regard for the average size of anions in the ion-polymer model (STRUCTON software program package [55]). The calculations were carried out for five K_e^{TS} values that were varied from 10^{-5} to 10^{-1} . The calculation results for the range of $0.52 \leq p \leq 98$ (20) in the right-hand plot in Fig. 8 (solid lines) were appended with an extrapolation to more silicic and polymerized compositions (dashed lines) conducted with the use of a polynomial dependence of i_{av} on p (Fig. 7).

These comparisons allowed us to formulate the following conclusions. First of all, it is worth mentioning that, in spite of the identical expressions for the polycondensation constant (25), this parameter characterizes two principally different thermodynamic models. In the Toop-Samis approach, O^{2-} ions are mixed in a virtual matrix of oxygen atoms (Fig. 6), whereas the ion-polymer model implies the mixing of this low-molecular product of reactions (5), (6) with the real species of the Si-O matrix: the SiO_4^{4-} , $Si_2O_7^{6-}$, $Si_3O_{10}^{8-}$,

and other ions. Because of this, equal K_e^{TS} values result in different concentrations of "free oxygen" (Fig. 8). These differences between the quasichemical and chemical models predetermine the interpretation of another important observation. The classic successions of $[O^{2-}]$ values in the model [24] display a monotonous decrease in the corresponding concentrations with increasing SiO₂ concentration (Fig. 8, left-hand plot), whereas simulations by the ion-polymer model suggest

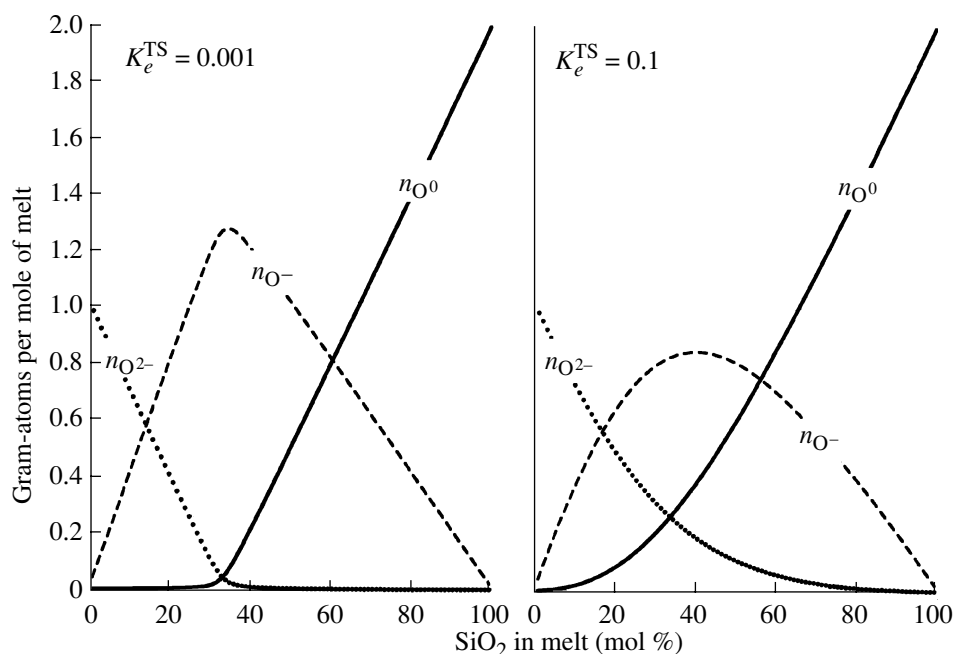


Fig. 6. Amount of oxygen quasispecies n_{O^0} , n_{O^-} , and $n_{O^{2-}}$ depending on the SiO_2 concentration in one mole of the MeO-SiO_2 system calculated by the Toop–Samis [24] method for two values of the polymerization constant (25).

The values $K_e^{\text{TS}} = 0.001$ and 0.1 model the presence of cations with a weakly (“Mg” or “Ca”) or strongly (“Fe”) pronounced polymerization effect. The equality of concentrations $n_{O^{2-}} = n_{O^0}$ characterizes melt of Me_2SiO_4 orthosilicates (33.3 mol % SiO_2).

the existence of a relative minimum in the concentration $x_{O^{2-}}$ at 40–45 mol % SiO_2 . The position of this minimum is consistent with predictions based on the polymer theory, which predicts that the starting gelization point of silicate liquid and a drastic decrease in the number of polymer species occur at a SiO_2 concentration equal to $3/7$, i.e., close to 43 mol % [28, 36].

Although the third conclusion is based on extrapolation results to more silicic compositions, it seems to be valid. The fact is that, because of the monotonous decrease in the number of free oxygen ions in the system (Fig. 6, $n_{O^{2-}}$), both of the thermodynamic models must yield zero concentrations $[\text{O}^{2-}]$ and $x_{O^{2-}}$ for pure SiO_2 . With regard for the aforementioned $x_{O^{2-}}$ minimum in the ion–polymer model, this implies the existence of another concentration extremum: a relative $x_{O^{2-}}$ maximum at 60–80 mol % SiO_2 . This conclusion is corroborated by our extrapolations (dashed line in Fig. 8). Obviously, the occurrence of such extrema in silicate systems is predetermined by the principal form of dependences (30) and the average size of the polyanions on the composition and are independent of the accuracy of the i_{av} extrapolation (Fig. 7). We attract attention to this conclusion for two reasons. First, the expected position of concentration maxima for $x_{O^{2-}}$ in MeO-SiO_2 systems falls into the liquid miscibility gap

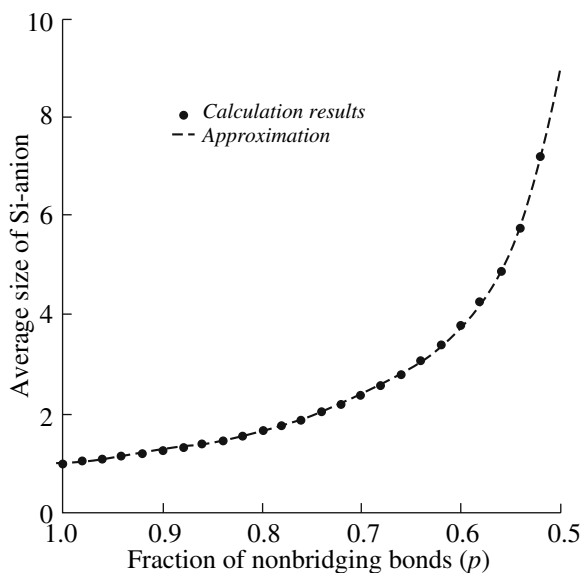


Fig. 7. Simulated dependence of the average size of a Si-anion on the fraction of nonbridging oxygen bonds in the polycondensated matrix.

The errors in i_{av} evaluations from the simulation results ($\pm 1\sigma$) vary from 0.002 ($p = 0.98$) to 0.35 ($p = 0.52$). The variations in this parameter are approximated by a sixth degree polynomial $i_{\text{av}} = 2261.75 - 17339.9p + 55407.4p^2 - 94141.2p^3 + 89572.9p^4 - 45218.6p^5 + 9458.67p^6$.

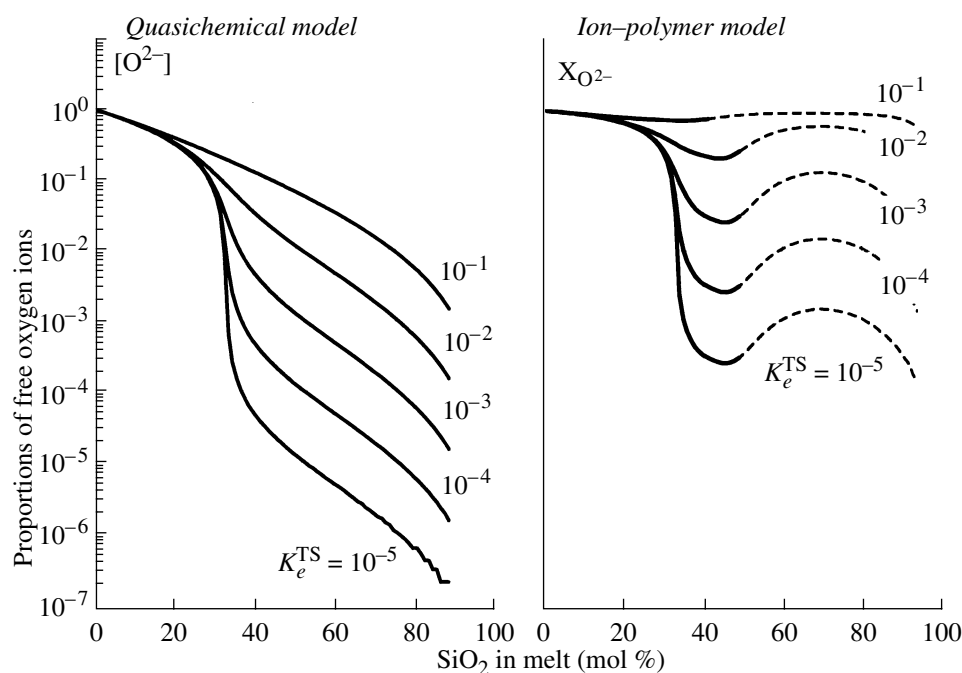


Fig. 8. Comparison of the concentrations of the free oxygen ion O^{2-} calculated for MeO–SiO₂ systems in the approximation of the quasichemical model [24] with regard for the results of MMD simulation by the STRUCTON software program package.

The calculations were carried out for five K_e^{TS} values that were varied from 10^{-5} to 10^{-1} . The $[O^{2-}]$ concentrations were calculated relative to the sum of quasispecies $n_{O^{2-}}/(n_{O_0} + n_{O^-} + n_{O^{2-}})$, which was evaluated by (23)–(25). The values of $x_{O^{2-}}$ was obtained using (30) and a polynomial dependence of the average size of anions i_{av} on p (Fig. 7). Solid lines in the right-hand plot show the results of calculations at $0.52 \leq p \leq 98$ (20). Dashed lines characterize extrapolations by Eq. (30) to the region of more silicic and polymerized compositions.

of silicate melt (see review in [14]). Thus, the occurrence of concentration maxima for free oxygen ions [or the activity of MeO (7)] implies the extremal behavior of the thermodynamic functions of mixing for the components of the polycondensated matrix and the principal possibility of a systematic description of immiscibility in silicate melts. Second, the formalism of the mathematical description of such minima and maxima can be applied in interpretations of the extremal solubility of oxides of transition metals (Fe, Ni, Co, and Cr), a phenomenon discovered in simple aluminosilicate systems at SiO₂ concentrations of 57 ± 2 mol % [66–68].

CONCLUSIONS

(1) A new statistical model is considered in application to the equilibrium structure (molecular–mass distribution, MMD) and the composition of polyanion complexes at a given distribution of Q^n structons in silicate melts [55]. The model is based on the representation of polymers in the form of a succession of Q^n species with various numbers of bridging bonds ($1 \leq n \leq 4$). The anion matrix is thereby described as a diversity of chains and cyclic complexes corresponding to the general formula $((Si_iO_{3i+1-j})^{2(i+1-j)-})$, where i is the num-

ber of Si atoms, and j is the number of self-cyclized bridging bonds in a given polymer. It was demonstrated that an ensemble of such Si–O species can be simulated by the Monte Carlo technique based on the known distribution of Q^n structons in silicate melt. This makes it possible to estimate the average size of the polyanions with regard for the constraints imposed onto the linkage of randomly selected structons via a single bridging Si–O⁰–Si bond. The model is utilized in the STRUCTON software program package designed for simulating the composition and proportions of polyanions in silicate melts at a given degree of their polymerization. The original code [55] is supplemented with a routine for the calculation of the random distribution of Q^n structons in the approximation of equal reaction ability of nonbridging bonds (version 1.2, 2007).

(2) The STRUCTON-1.2 program package was used to model the MMD of polyanions in the interval $0.52 \leq p \leq 98$, where p is the fraction of nonbridging bonds in the Si–O matrix. Each calculation was carried out for $N = 10000$ of initial Q^n monomers, and the specified p values corresponded to a series of 50 calculations. This allowed us to evaluate the reproducibility and statistical parameters of the calculated MMD within broad ranges of states of the polymerized

matrix, from the predominance of the SiO_4^{4-} monomer and a minor amount of the $\text{Si}_2\text{O}_7^{6-}$ ion to the gelization point, which is marked by an unlimited increase in the anion complexes. The calculation results yielded the mole fractions of individual anions and cyclic groups, which are combined according to the equal number of cyclized end-positioned bonds [20, 34]. It was determined that the average amount of silicate complexes (of 10^4 original monomers) systematically decreases from 9480 at $p = 0.98$ to 1390 at $p = 0.52$, and the average number of their types simultaneously increases from three (SiO_4^{4-} , $\text{Si}_2\text{O}_7^{6-}$, and $\text{Si}_3\text{O}_{10}^{8-}$) to 153. It was demonstrated that chain anions of size $i \geq 25$ –28 do not form even in the most polymerized matrix, and the factor limiting their increase is cyclization, a process related to the closure of bridging bonds. The average size of the polyanions i_{av} in this range of p increases from 1 to 7.2.

(3) One option of the STRUCTON software program package combines the simulation of MMD in silicate melts with the formalism of the theory [24] for MeO – Me_2O – SiO_2 systems. This enables the simulation of the mole fraction of the O^{2-} ion relative to the overall amount of anions in melts of specified composition at certain values of the polymerization constant (20, 23–35, 30). For five values $10^{-5} \leq K_e^{\text{TS}} \leq 10^{-1}$, we compared the dependences of the O^{2-} concentration on the SiO_2 concentration, which were calculated for MeO – SiO_2 systems in the approximation of the Toop–Samis quasichemical approach and the presented ion–polymer model. It is demonstrated that, taking into account the distribution and average size of the polymerized complexes, results in two extrema in the O^{2-} concentration. One of them is a relative minimum at 40–45 mol % SiO_2 and corresponds to the initial gelization stages of the polycondensated silicate matrix. The other one is a maximum of $x_{\text{O}^{2-}}$, which is predicted for SiO_2 concentrations of 60–80 mol %.

The results of MMD simulations presented in this publication and the interpretation of the O^{2-} concentration as the activity of metal oxides a_{MeO}^I propose a natural avenue for the further development of the theory of silicate melts, which combines the capability of the ion–polymer model and some propositions of the theory of associated solutions. The further development of statistical modeling techniques in application to silicate melts involves accounting for the presence of aluminooxygen species and the examination of the effect of volatile components (H_2O and CO_2) on the degree of polymerization of the Si–O matrix. An important element of these models is the possibility of taking into consideration disproportionation reactions and the unequal reaction ability of Q^n structons of different types. These approaches have a great potential for the development

of a new class of realistic and consistent models for the crystallization and melting in magmatic and metallurgical systems.

ACKNOWLEDGMENTS

The authors thank A.A. Borisov for valuable comments on the manuscript. This study was financially supported by the Russian Foundation for Basic Research, project nos. 08-05-00194 and 05-05-64906.

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