

MODELING OF ACID-BASE PROPERTIES OF BINARY ALKALI-SILICATE MELTS

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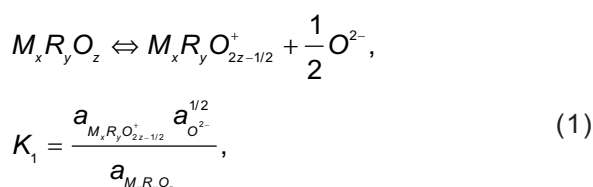
Abstract. The generalized model of the acid-base interaction in oxide melts was used to describe the properties of alkali-silicate melts. A model for numerical simulation of dissociation constants was proposed and verified for sodium-silicate and potassium-silicate melts. The applicability of a number of methods for the optimization of the compositional dependence of the oxide basicity (in pO terms) is compared for Na_2O-SiO_2 and K_2O-SiO_2 melts.

1. INTRODUCTION

Investigations and modeling of acid-base properties of glass-forming melts containing different oxides are a point of key interest in the high-temperature physical chemistry. The problem of the experimental determination of the oxide melt basicity, formulated for the first time by Lux in 1939 [1], remains actual up to the present time [2-5]. Nowadays, the basicity of oxide melts is conventionally considered as the activity of O^{2-} oxygen ions or pO -index ($pO = -\lg a_{O^{2-}}$) [1, 3, 5], which can be determined by high-temperature EMF (Electro Moving Forces) method and then normalized using the specially developed procedures [3, 6].

A generalized model of the acid-base interaction in oxide melts was proposed in [3,6] to interpret the experimental data. According to this model, any oxygen-containing substance in the melt (an oxide, an electroneutral or charged grouping) dissociates with a detachment of 1/2 mole of oxygen ion O^{2-} . So the contribution of this substance to the

total melt basicity is defined by its dissociation constant:



where K_1 is the dissociation constant and a_i is the activity of the i -th substance.

Generally, reaction (1) is the unit act of the acid-base interaction.

Numerical simulation is one of the methods to interpret the experimental data and to analyze the acid-base interactions in oxide melts. The aim of this method is to determine the dissociation constants for a set of structural-chemical groupings forming in the melts with a different chemical nature. An optimization method should be used in these simulations, which minimizes the deviations in the

compositional dependence of the melt basicity calculated using Eq. (1) from those measured experimentally (criterion function). The least square method was used earlier in [3-5] for this optimization within the simulations performed for the alkali-silicate, alkali-borate and alkali-germanate melts. However, some more precise methods of data optimization can be suggested for this task such as nonlinear method of least squares, simplex-method, and quasi-Newton method.

The aim of the present paper is to compare the different optimization methods in the simulations of the compositional dependence of the basicity (in pO terms) for the Na_2O - SiO_2 and K_2O - SiO_2 melts.

2. INITIAL DATA

It is seen from Eq. (1) that the following set of equations can be considered for potassium-silicate melts:

$$\begin{aligned}
 SiO_2 &\Leftrightarrow SiO_{3/2}^+ + \frac{1}{2}O^{2-}, \\
 K_2 &= \frac{x_{SiO_{3/2}^+} x_{O^{2-}}^{1/2}}{x_{SiO_2}}, \\
 K_2Si_4O_9 &\Leftrightarrow K_2Si_4O_{18/2}^+ + \frac{1}{2}O^{2-}, \\
 K_3 &= \frac{x_{K_2Si_4O_{18/2}^+} x_{O^{2-}}^{1/2}}{x_{K_2Si_4O_9}}, \\
 K_2Si_2O_5 &\Leftrightarrow K_2Si_2O_{9/2}^+ + \frac{1}{2}O^{2-}, \\
 K_4 &= \frac{x_{K_2Si_2O_{9/2}^+} x_{O^{2-}}^{1/2}}{x_{K_2Si_2O_5}}, \\
 K_2SiO_3 &\Leftrightarrow K_2SiO_{5/2}^+ + \frac{1}{2}O^{2-}, \\
 K_5 &= \frac{x_{K_2SiO_{5/2}^+} x_{O^{2-}}^{1/2}}{x_{K_2SiO_3}}, \\
 K_2O &\Leftrightarrow 2K^+ + O^{2-}, \\
 K_6 &= \frac{x_{K^+}^2 x_{O^{2-}}}{x_{K_2O}}.
 \end{aligned} \tag{2-6}$$

The equation of charge conservation is:

$$\begin{aligned}
 2x_{O^{2-}} &= x_{K^+} + x_{SiO_{3/2}^+} + x_{K_2Si_4O_{18/2}^+} + \\
 &x_{K_2Si_2O_{9/2}^+} + x_{K_2SiO_{5/2}^+}.
 \end{aligned} \tag{7}$$

According to the above generalized model, the of acid-base interaction between the components of the binary melt are generally affected by the reaction between the carrier of acidic properties (SiO_2) and the carrier of alkaline properties (K_2O). Note that all the participants of the reactions in the melt (initial components and intermediate compounds) make their contributions in the basicity of the reaction product (the glass-forming melt) proportionally to their dissociation constants. The K_2 value is rather low ($6.32 \cdot 10^{-11}$) for SiO_2 ; it is defined by normalization conditions for the O^{2-} activity. In contrast, the K_6 value for the main component of the reaction mixture, K_2O , is expected to be high. Since SiO_2 does not change its coordinational oxygen surrounding in intermediate compounds, the relation for the dissociation constants (2-6) should meet the following condition:

$$K_2 < K_3 < K_4 < K_5 < K_6. \tag{8}$$

A similar set of equations can be written for sodium-silicate melts with respect to the fact that two structural-chemical groupings $Na_2O \cdot 2SiO_2$ and $Na_2O \cdot SiO_2$ are present in these melts:

$$\begin{aligned}
 SiO_2 &\Leftrightarrow SiO_{3/2}^+ + \frac{1}{2}O^{2-}, \\
 K_2 &= \frac{x_{SiO_{3/2}^+} x_{O^{2-}}^{1/2}}{x_{SiO_2}}, \\
 Na_2Si_2O_5 &\Leftrightarrow K_2Si_2O_{9/2}^+ + \frac{1}{2}O^{2-}, \\
 K_9 &= \frac{x_{Na_2Si_2O_{9/2}^+} x_{O^{2-}}^{1/2}}{x_{Na_2Si_2O_5}}, \\
 Na_2SiO_3 &\Leftrightarrow Na_2SiO_{5/2}^+ + \frac{1}{2}O^{2-}, \\
 K_{10} &= \frac{x_{Na_2SiO_{5/2}^+} x_{O^{2-}}^{1/2}}{x_{Na_2SiO_3}}, \\
 Na_2O &\Leftrightarrow 2Na^+ + O^{2-}, \\
 K_{11} &= \frac{x_{Na^+}^2 x_{O^{2-}}}{x_{Na_2O}}.
 \end{aligned} \tag{2,9-11}$$

Table 1 presents the dissociation constants obtained earlier in [3] using the linear least square optimization method.

One can see from this table that several sets of the roots (set constants K_i in Table 1 for the systems Na_2O - SiO_2 and K_2O - SiO_2) satisfy for the numerical solution of the sets of exponential equations

Table 1. Dissociation constants of oxides and structural-chemical groupings of alkali-silicate melts [3].

Oxide, grouping	K_1	Oxide, grouping	K_1
SiO_2	$6.32 \cdot 10^{-11}$	$2\text{Li}_2\text{O} \cdot \text{SiO}_2$	$90 \cdot 10^{-11}$
$\text{Li}_2\text{O} \cdot 2\text{SiO}_2$	$9.7 \cdot 10^{-11}$	$\text{K}_2\text{O} \cdot 2\text{SiO}_2$	$100 \cdot 10^{-11}$
$\text{Li}_2\text{O} \cdot \text{SiO}_2$	$21 \cdot 10^{-11}$	$\text{Na}_2\text{O} \cdot \text{SiO}_2$	$200 \cdot 10^{-11}$
$\text{Na}_2\text{O} \cdot 2\text{SiO}_2$	$26 \cdot 10^{-11}$	$\text{K}_2\text{O} \cdot \text{SiO}_2$	$4300 \cdot 10^{-11}$
$\text{K}_2\text{O} \cdot 4\text{SiO}_2$	$70 \cdot 10^{-11}$		

(2-6) and (9-11). Thus, the aim of our simulations was to find a set of roots which allows to describe a required function with maximum precision.

3. REALIZATION OF CALCULATION

The sum of squares of discrepancies between the experimental and calculated values of pO was used as a criterion function:

$$F = \sum_{i=1}^n (pO^{\text{эксп}} - pO^{\text{рас}})^2 \quad (12)$$

The experimental values of pO from [3] and compositional dependencies of the concentration of structural-chemical groupings in alkali-silicate melts from [7-9] were used as initial data for our simulations (Fig.1-3).

The data optimization was carried out using three methods:

- 1) The nonlinear method of least squares;
- 2) The quasi-Newton method;
- 3) Nelder-Midd's simplex-method.

Three sets of the dissociation constants were chosen as an initial approximation for sodium-silicate melts:

Set A – the values of K obtained in [3]: $6.32 \cdot 10^{-11}$, $26 \cdot 10^{-11}$, $200 \cdot 10^{-11}$, 0 (the activity of sodium oxide approaches 0);

Set B – the values of K obtained under the assumption that all the melt in the point of composition corresponding to the composition of a structural-chemical grouping consists completely of this grouping: $6.32 \cdot 10^{-11}$, $1.2 \cdot 10^{-11}$, $2.236 \cdot 10^{-11}$, 0;

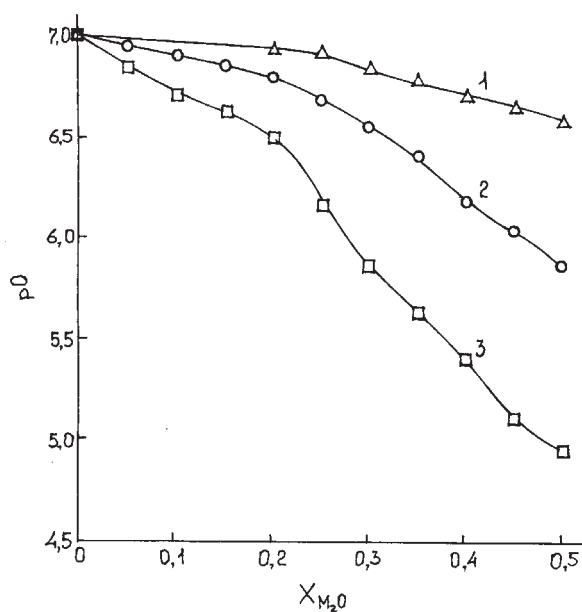


Fig.1. Experimental data on pO vs melt composition dependence in: 1 – $\text{Li}_2\text{O} \cdot \text{SiO}_2$, 2 – $\text{Na}_2\text{O} \cdot \text{SiO}_2$, 3 – $\text{K}_2\text{O} \cdot \text{SiO}_2$ melts.

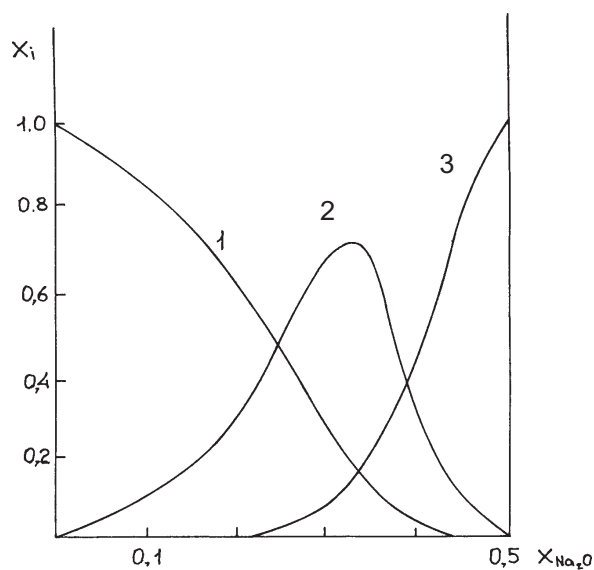


Fig.2. Chemical structure of the melts for the $\text{Na}_2\text{O} \cdot \text{SiO}_2$ system. 1 – SiO_2 , 2 – $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$, 3 – $\text{Na}_2\text{O} \cdot \text{SiO}_2$.

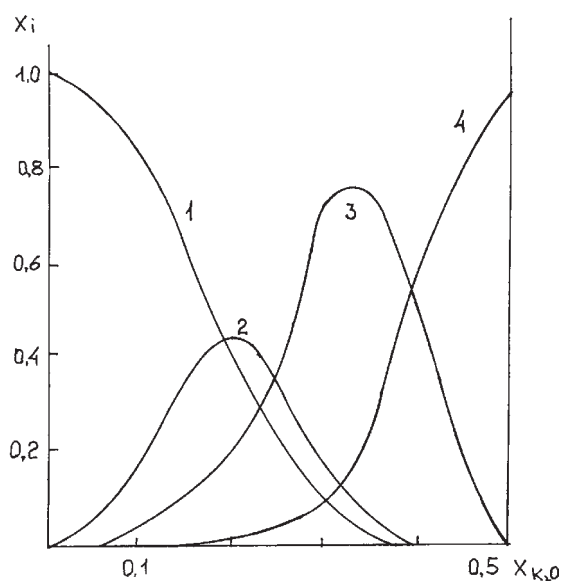


Fig. 3. Chemical structure of the melts for the K_2O - SiO_2 system. 1 – SiO_2 , 2 – $K_2O \cdot 4SiO_2$, 3 – $K_2O \cdot 2SiO_2$, 4 – $K_2O \cdot SiO_2$.

Set C – the values of K chosen at will in the range between set A and set B: $6.32 \cdot 10^{-11}$, $20 \cdot 10^{-11}$, $100 \cdot 10^{-11}$, 0.

An initial approximation for potassium-silicate melts was made in a similar way. Moreover, the following limitation (8) was set on the values of K : $K_1 < K_2 < \dots < K_n$. It means that the basicity values of all intermediate compounds forming in this system lie in the range between the basicity values of the initial reagents – the most acidic SiO_2 and the most alkaline Na_2O (K_2O).

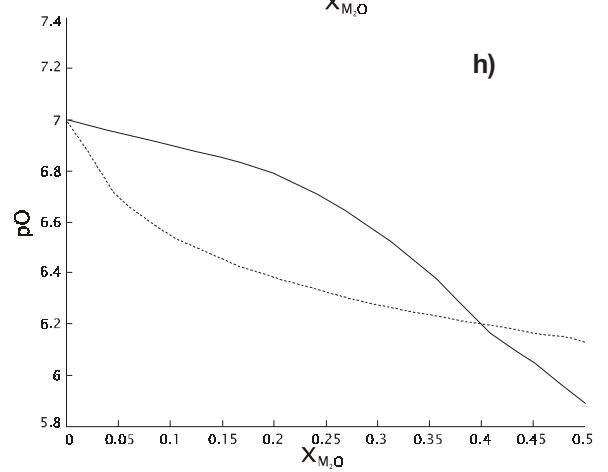
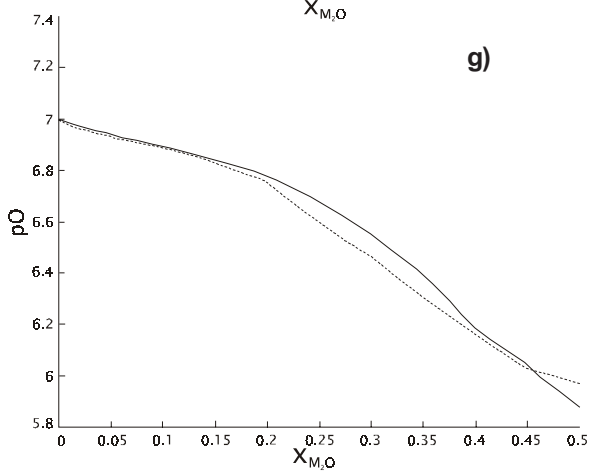
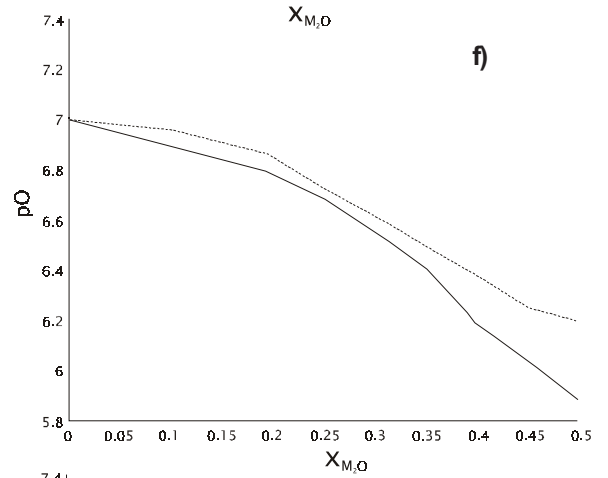
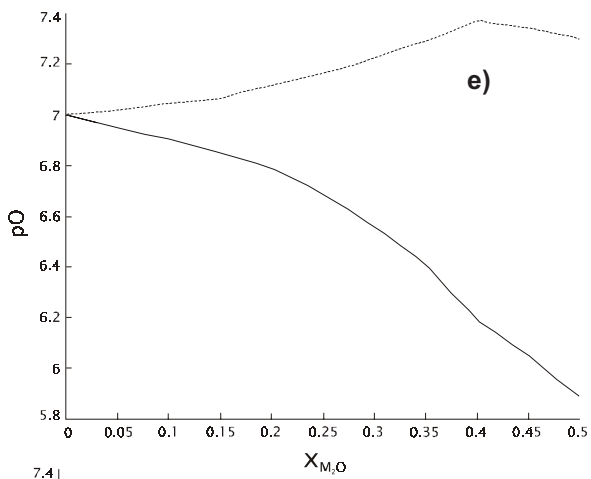
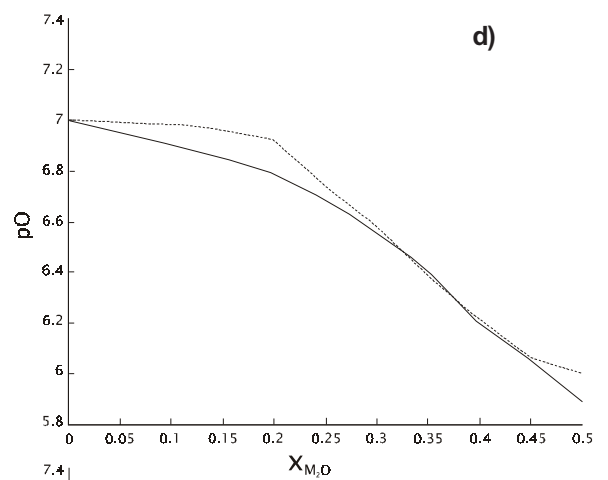
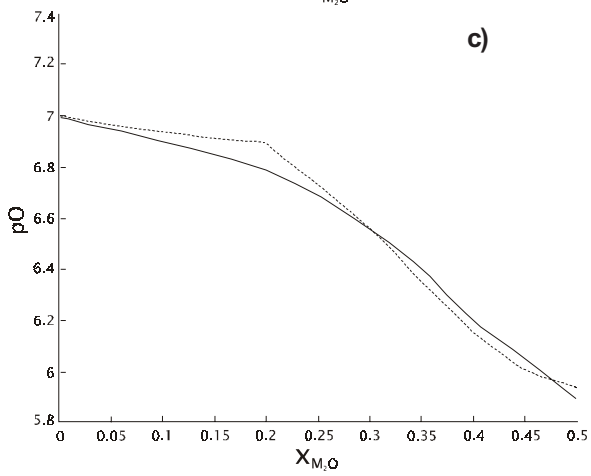
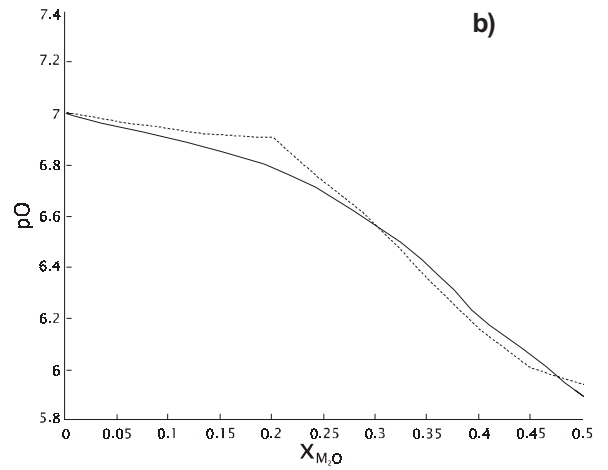
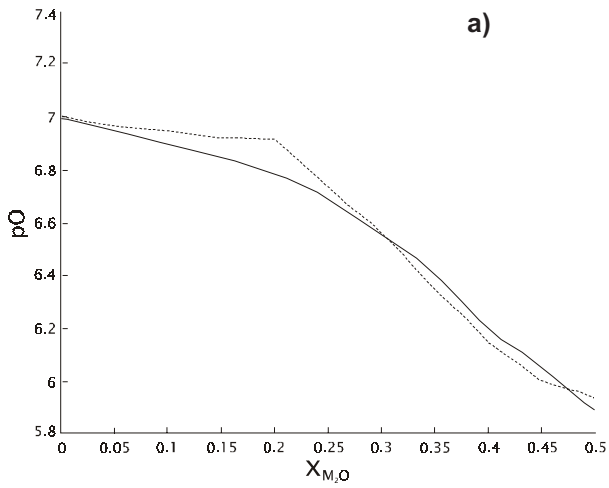
Optimization of the data was carried out in programming environment MATLAB using the internal programming language of a system (M-language). M-language was specially designed for the solution of mathematical problems. It has high-power and diverse graphic possibilities and many specific op-

Table 2. Results of optimization of the data on basicity of sodium-silicate melts.

Methods of optimization	Initial values, $\times 10^{-11}$	Final values, $\times 10^{-11}$	The sum of squares of discrepancies (F)	Number of iterations
nonlinear method	[26, 200, 0]	[23.19, 239.54, 0.0025]	$4.7204 \cdot 10^{-14}$	52
nonlinear method	[1.2, 2.236, 0]	[0, 237.7, 25.7]	$4.7114 \cdot 10^{-14}$	44
nonlinear method	[20, 100, 0]	[25, 238.13, 0.2]	$4.7171 \cdot 10^{-14}$	39
quasi-Newton method	[26, 200, 0]	[13.5, 201.6, 0]	$1.0345 \cdot 10^{-13}$	7
quasi-Newton method	[1.2, 2.236, 0]	[1, 2.338, 0]	$2.8758 \cdot 10^{-12}$	5
quasi-Newton method	[20, 100, 0]	[20, 100, 0]	$6.4804 \cdot 10^{-13}$	5
simplex-method	[26, 200, 0]	[26, 210, 9.8]	$8.8193 \cdot 10^{-14}$	44
simplex-method	[1.2, 2.236, 0]	[1.2, 2.3, 246.4]	$7.0104 \cdot 10^{-13}$	53
simplex-method	[20, 100, 0]	[20, 105, 111.5]	$3.2740 \cdot 10^{-13}$	52

Table 3. Results of optimization of the data on basicity of potassium-silicate melts.

Methods of optimization	Initial values, $\times 10^{-11}$	Final values, $\times 10^{-11}$	The sum of squares of discrepancies (F)	Number of iterations
nonlinear method	[70, 100, 4300, 0]	[1, 1, 5064, 0.0026]	$1.2888 \cdot 10^{-11}$	111
nonlinear method	[0.565685, 1.1989495, 2.236, 0]	[1.8, 1, 5064, 0.002]	$1.2888 \cdot 10^{-11}$	132
nonlinear method	[35, 50, 2150, 0]	[1.68, 1, 5063, 1]	$1.2890 \cdot 10^{-11}$	150
quasi-Newton method	[70, 100, 4300, 0]	[0, 0, 5031, 0]	$1.2883 \cdot 10^{-11}$	6
quasi-Newton method	[0.565685, 1.2, 2.236, 0]	[0.565685, 1.2, 2.236, 0]	$1.8675 \cdot 10^{-10}$	9
quasi-Newton method	[35, 50, 2150, 0]	[35, 50, 2150, 0]	$4.5956 \cdot 10^{-11}$	10
simplex-method	[70, 100, 4300, 0]	[70, 100, 4516, -145]	$1.4590 \cdot 10^{-11}$	423
simplex-method	[0.565685, 1.2, 2.236, 0]	[0.565685, 1.2, 2.348, 4548]	$6.6560 \cdot 10^{-11}$	80
simplex-method	[35, 50, 2150, 0]	[35, 50, 2258, 1747]	$3.2939 \cdot 10^{-11}$	441



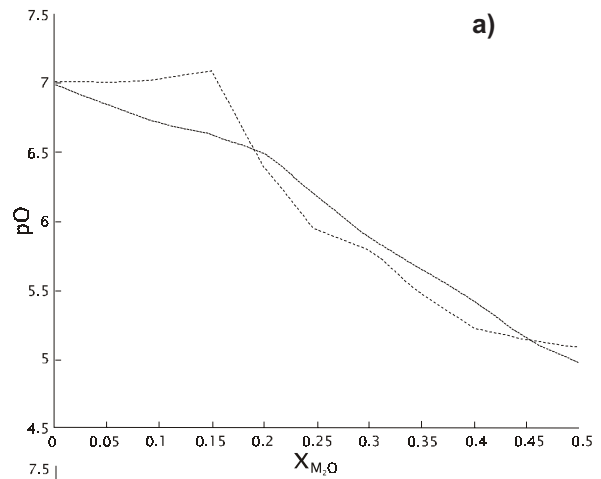
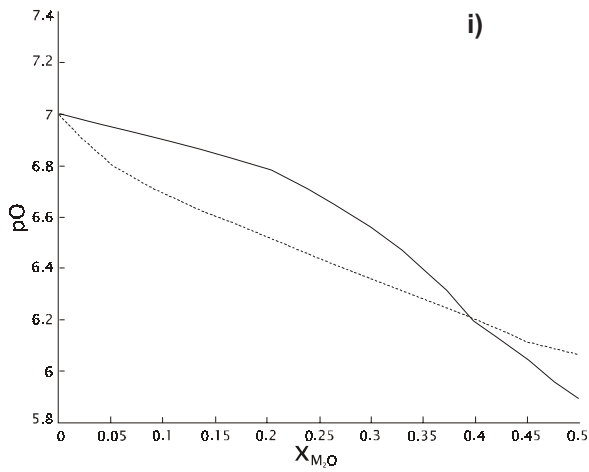
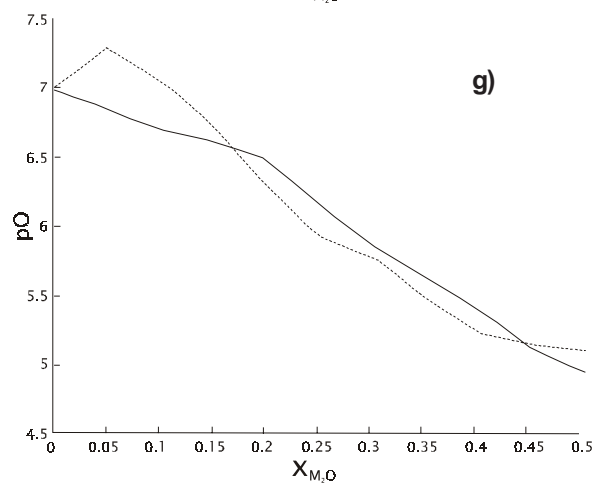
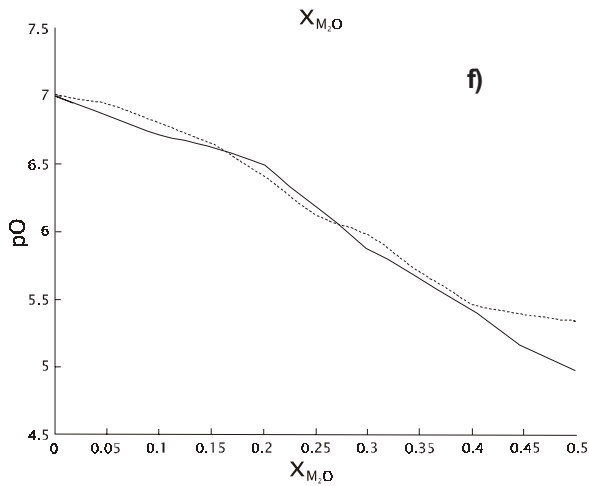
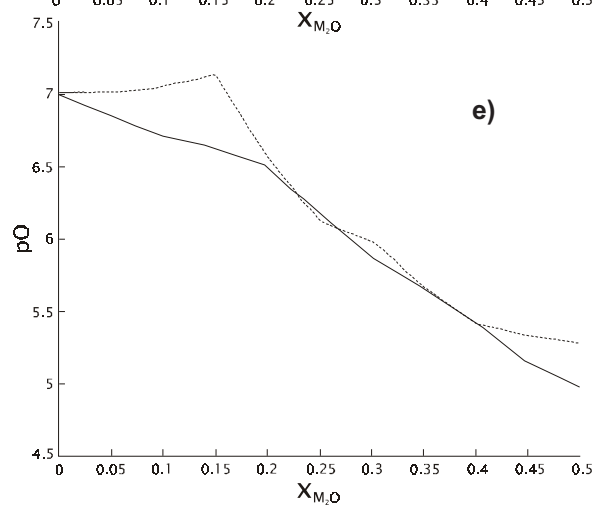
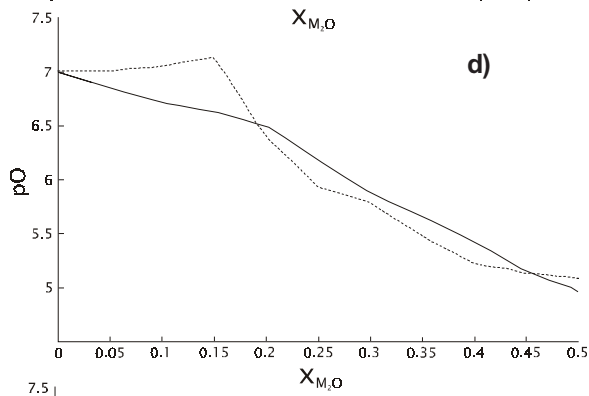
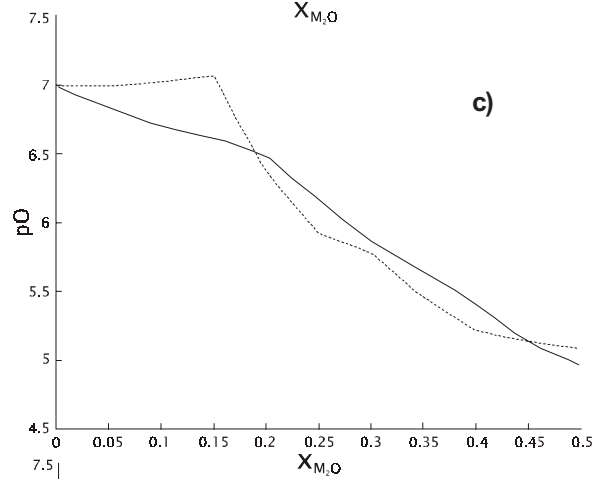
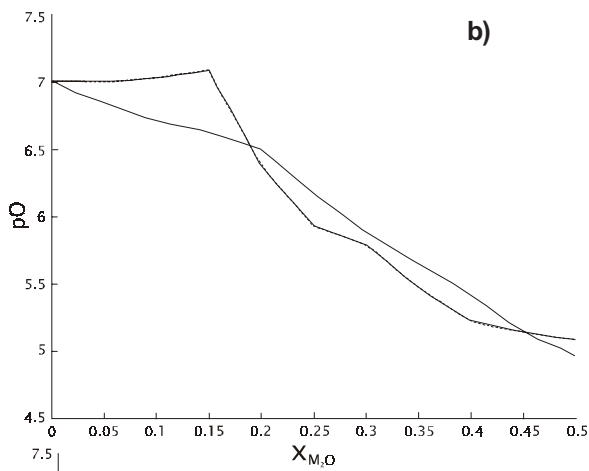


Fig. 4. Results of optimization of the data on basicity of sodium-silicate system (solid line – experiment, dot line – calculation). a–c – nonlinear method, d–f – quasi-Newton method, g–i – simplex-method.



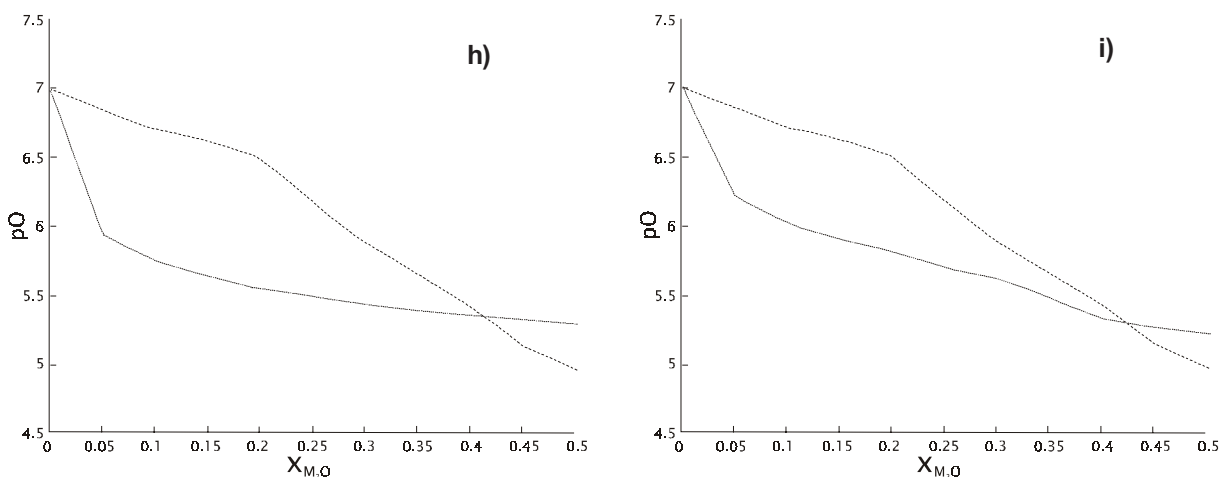


Fig. 5. Results of optimization of the data on basicity of potassium-silicate system (solid line – experiment, dot line – calculation). a–c – nonlinear method, d–f – quasi-Newton method, g–i – simplex-method.

erations that allow to carry out a large volume of calculations with compact expressions. The text of the program used in present work for calculations and data optimization can be seen at <http://www.isc.nw.ru>.

The results of optimization are shown in Tables 2, 3 and Figs. 4, 5.

One can see from Figs. 4 and 5 that some discrepancies between the calculated and experimental data are observed in the range of 0.45–0.5 mol.% of alkali oxide. They can be due to possible presence of orthosilicates in the system, since these compounds contain more alkali oxide than metasilicates. This possibility was not accounted for in the initial data used in our simulations, meanwhile orthosilicates can make a significant contribution to the melt basicity even at low orthosilicate concentration. This can lead to an overestimation of the values of metasilicate dissociation constants and to an underestimation of the calculated values of pO -indexes.

The dissociation constant of SiO_2 ($6.32 \cdot 10^{-11}$) is not shown in Tables 2 and 3 because it was always preset with respect to the normalization requirement of pO -scale; therefore, it was not optimized within the described procedure.

As can be seen from the Tables, there is a great number of the roots fitting the equations solution. At that the criterion function F takes different values. One can see that the minimal values of this function were obtained using the nonlinear least square method. However, the dissociation constants

do not satisfy the limitation (8) in this case. The quasi-Newton approach give rise to the F -function values higher by an order of magnitude, however it agree with the condition set in limitation (8). Simplex-method describes the experimental data quite well only if we use the set A as an initial approximation for calculations, i.e. we use the pre-optimized dissociation constants.

Thus, it can be concluded that the data optimization should be carried out in two stages: using the nonlinear least square method at the first stage to obtain the minimal values of F -function and by the quasi-Newton method at the second stage to get the values of dissociation constants satisfying limitation (8).

4. CONCLUSIONS

1. It was shown that the surface of the optimization function for the compositional dependence of the basicity of alkali-silicate melts is complicated and contains a large quantity of local minima.
2. To perform simulations consistently, it is necessary to use the two-stages optimization procedure: first using nonlinear least square method and then applying quasi-Newton method.
3. The limitation set on the values of dissociation constants should be rigid enough and should be expressed as a numerical inequality.

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