

УДК 541.451–143

PHYSICOCHEMICAL PROPERTIES OF POLYMERIC OXIDE MELTS AND THEIR CORRELATION WITH BASIC STRUCTURAL COMPONENTS

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Article was presented July 21, 2005

Introduction

The physicochemical properties of disorder condensed substances, in particular, polymeric silicate melts are determined by their structure. The basically structural units in them are silicate–oxygen anions of a various degree of complexities, which are taking place in chemical balance among themselves and "free" ions of oxygen. Complex anions represent repeating parts silicate–oxygen tetrahedral, formed as a result of reaction polymerization with the participation of monomers. They can have both chained and ring configuration.

Each structural component of the melts in MeO–SiO₂ system has been estimated numerically in dependence from number of monomers and charge, using Randić's χ — criterion [1], calculated by the equation

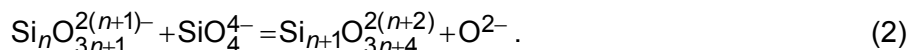
$$\chi = \sum 1/(v_i v_j)^{1/2}, \quad (1)$$

where v_i and v_j are the numbers of bonds originating at a given and neighboring graph vertices, and the summation is over all bonds connecting vertices.

The standard Gibbs energies of formation of molten silicates, borates, phosphates, titanates, aluminates and ferrites from super cooled liquid oxides (ΔG_{sl}^0) at the temperatures of fusion of the compounds. The values were calculated by the equation based on the assumption of equality the heat capacities of solid and supercooled oxides [2]. The values ΔG_T^0 were determined by the Temkin–Shvartsman's method from the data of handbooks.

As well it is known, that the main structure elements of the silicate melts are silicate–oxygen ions of the different degree of complication, based on the chemical equilibration between themselves and "free" ions of oxygen. The complex anions present as a reiterative chain of silicate–oxygen tetrahedrons, forming as a result of the polymerization reactions with the participation of monomers SiO₄^{4–}.

An interaction of complexes with each other leads to complication of their structure and is accompanied by separation into the melt of "free" oxygen anions



The charges of complex anions and "free" oxygen anions are indemnified by the positive charges of metallic ions. On the basis of the stated theoretical positions a quantitative scale of the short-range order structure elements in oxide melts has been developed [3] and connected with the standard Gibbs energies of formation [2]. Further, as a first approximation we limited only with those structural elements, which in independent researches by a method trimethylsilylation [4] have been revealed early in the binary systems.

We may concern to them "free" oxygen — O^{2-} , monomers — SiO_4^{4-} , the chains — $Si_2O_7^{6-}$, $Si_3O_{10}^{8-}$, rings — $Si_3O_9^{6-}$, $Si_4O_{12}^{8-}$, $Si_6O_{18}^{12-}$. More larger formations have designated as $(SiO_2)_i$. Bridge — O^0 and non-bridge — O^- oxygen ions also correspond the own numerical meanings (tabl. 1).

The dependence of any of physicochemical property, for example, surface tension or density, from concentration at certain temperature and pressure is determined by another numerical sequence. Thus, the task of revealing of correlation connections between properties and parameters of structure is reduced to establishing of coefficients describing the contribution of this or that element of structure into a certain property. This task was solved by a method of multiple regressions taking into account the presenting in the melt of determined concentration structural elements.

Table 1

The quantitative parameters of anion elements in disorder oxide melts

n or m^*	$\chi_{O^{m-}}$	$\chi_{Si_nO_{3n+1}^{2(n+1)-}}$	$\chi_{Si_nO_{3n}^{2n-}}$
		$(n+1)/\sqrt{1.5} + (n-1)/\sqrt{2}$ at $n \geq 1$	χ_n at $n \geq 3$
0	0.075	—	—
1	0.092	1.633	—
2	0.109	3.157	—
3	—	4.680	4.571
4	—	6.020	6.094
5	—	7.727	7.618
6	—	9.252	9.142

* m — charge of anion; n — number of tetrahedral in a chain or ring

It is known, that the melt SiO_2 is completely polymerized and represents spatial grid of tetrahedral SiO_4 , connected through bridge oxygen. In binary system $PbO-SiO_2$ ($CaO-SiO_2$) in an interval of concentrations up to 33 wt. % SiO_2 there are mainly monomers, "free" ions of oxygen O^{2-} and cations of metal Pb^{2+} (Ca^{2+}). In the melt of pure metallic oxide are available only anions of "free" oxygen and cations Pb^{2+} (Ca^{2+}). Thus, for three concentrations their structural elements presenting in the system are known.

The experiment does not give an opportunity to reveal the contribution of concrete structural unit to the certain property in the system (for example, density). Hence, for finding the factors of linear regression it is necessary to attract the additional items of information on distribution of structural units in melts of various concentrations. The decision of this task has been carried out, using the opportunities of polymeric models [5, 6].

Let us designate the size of i -fragment of structure (Fr_i) as

$$Fr_i = C_i \lg(\chi_i), \quad (3)$$

where C_i — its concentration for the melt of certain compound.

Having two data sets, first of which — concentration dependence of structural sensitive property of melt, and second — its fragments, we have connected them as follows

$$\lg(1/Y_j) = K_{0j} + \sum_{i=1}^I K_{ij} Fr_{ij}, \quad (4)$$

in which Y_j — values of structural sensitive properties, Fr_{ij} — numerical meanings of fragments (see table 2) with appropriate K_{ij} — weight coefficients, I — a number of basic elements of structure.

In this equation required values are the factors K_{ij} and K_{0j} . In order to find them, we have written down system of the equations, having taken advantage concentration dependences of structural sensitive property and elements of structure

$$\begin{aligned} \lg(1/Y_1) &= K_{01} + \sum_{i=1}^I K_{i1} Fr_{i1}, \\ &\dots\dots\dots, \\ \lg(1/Y_p) &= K_{0p} + \sum_{i=1}^I K_{ip} Fr_{ip}, \end{aligned} \quad (5)$$

where p — is a number of equations in the system.

Table 2

The meaning coefficients of the linear regression

Element of structure	i	$\lg \chi_i$	$K_{i(p)}$ PbO—SiO ₂	$K_{i(v)}$ PbO—SiO ₂	$K_{i(\sigma)}$ PbO—SiO ₂	$K_{i(p)}$ CaO—SiO ₂	$K_{i(v)}$ CaO—SiO ₂
— — —	0	—	−3,664	4,931	−2,405	−3,391	1,601
O ⁰	1	−1,036	−0,009	0,136	—	−0,013	—
O [−]	2	−1,125	0,080	—	−0,043	0,053	−0,094
O ^{2−}	3	−0,963	0,043	−0,343	−0,138	−1,012	1,664
SiO ₄ ^{4−}	4	0,213	−0,721	−1,344	—	−0,560	0,682
Si ₂ O ₇ ^{6−}	5	0,499	1,197	1,476	−0,528	0,421	—
Si ₃ O ₁₀ ^{8−}	6	0,670	−2,320	—	1,932	−0,554	—
Si ₃ O ₉ ^{6−}	7	0,660	—	−2,014	—	—	0,413
Si ₄ O ₁₂ ^{8−}	8	0,785	—	—	—	—	—
Si ₆ O ₁₈ ^{12−}	9	0,882	—	—	—	—	—
(SiO ₂) _{i}	10	0,905	—	−0,134	—	—	0,076
Me ²⁺	11	−0,050	3,113	16,290	−3,314	0,840	−0,677

Having calculated coefficients of regression, on their values determined the contribution of each fragment to physicochemical property of system.

This approach was used for research rather fully investigated silicate systems. In particular, the density and surface tension data in systems PbO—SiO₂ at 1273 K and CaO—SiO₂ at 1973 K are available in literature [7]. Using distribution of the structure elements we have chosen 10 points with a step 0.1 by molecular share of SiO₂ and have constructed the system of equations (5), in which the right part takes into account influence of concentration melt on a quantity of various structural units, and left one — a concentration dependence of structural sensitive property.

Let's note, that the distribution of non-bridge, bridge and "free" oxygen and silicate anions were taken into account separately, not uniting these concentration dependences in one equation. In result we have received twenty equations (p), containing twelve unknown values in everyone, eleven (I) from which are the factors of the basic structure elements fragments (K_{ij}) and a free member in the equation (K_{0j}).

The decision of superfluous system have carried out under condition: $p > I + 1$ with the advanced algorithm [8] by the method of the least squares.

The results of account in systems PbO—SiO₂ and CaO—SiO₂ are given in table 2 and the concentration dependences of density and surface tension for PbO—SiO₂ are represented in fig. 1, 2.

As it can be seen from the table 2 some values of the factors K_{ij} are absent. In initial approximation all weight multipliers were taken into account, however, at the subsequent specification of accounts they have appeared insignificant.

At the present time the polymeric model does not allow to estimate the difference of concentrations of the structural elements in the surface layer and in volume. Thereof at the definition of contribution of the structure elements in the surface tension and density by above described method we took into account the changes of their concentration in the volumes of the melts. It has resulted in some discrepancy of the skilled and settlement meanings of properties.

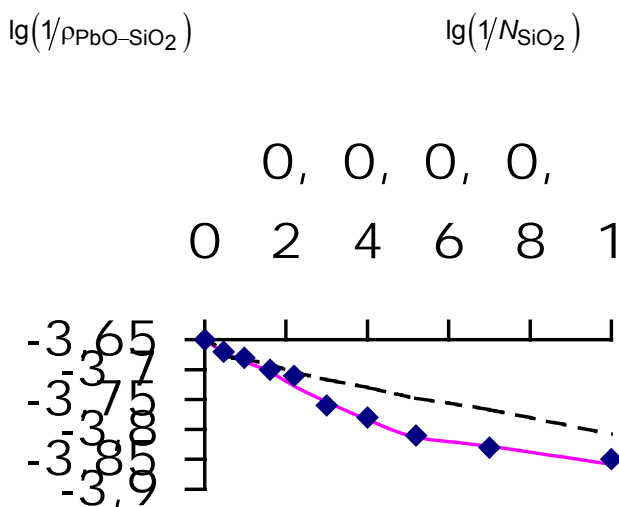


Fig. 1. The concentration dependence of the density in the system PbO—SiO₂:
points — experimental data [7]; continuous line — account; dashed line — account without all forms of oxygen

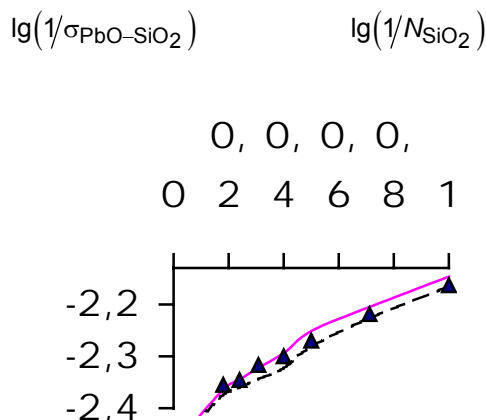


Fig. 2. The concentration dependence of the surface tension in the system PbO—SiO₂:
points experimental data [7]; continuous line — account; dotted line — account without bridge oxygen

Thus, as it is seen, with the help of the linear equation multifactor regression it is possible to manage two sets of numbers, describing properties (density ρ , molar volume V , surface tension σ) and their structure. Similarly, it is possible to describe another physical or physicochemical properties, such as conductivity, viscosity etc., and as well to distribute the given approach to multicomponent systems, which structure includes complex formation elements.

Conclusion

So, the approach, used in organic chemistry, is applied for definition of the contribution of the elements of structure in high molecular melts into their selective activity for revealing correlation dependencies such as "structure–property" in the polymeric systems PbO—SiO₂ and CaO—SiO₂.

References

1. Randić M. On Characterization of Molecular Branching // J. Amer. Chem. Soc., 1975. Vol. 97, № 23. P. 6609—6615.
2. Novikov V.K., Spiridonov M.A., Zinovieva I.S. Thermochemical Basicity Indexes of Oxides// Russian J. of Physical Chemistry, 1998. Vol. 72, № 2. P. 173—176.
3. Spiridonov M.A., Novikov V.K., Zinovieva I.S. Elements of Structure in Chemical Thermodynamic of Oxide Melts // Physical Chemistry and Technology of Nonorganic Materials, 1998. № 2. P. 50—54: http://www.sci.ac.ru/news/1998_2/2—3—5.pdf.
4. Smart R.M., Glasser F.P. Silicate anion constitution of lead silicate glasses and crystals// Phys. a. Chem. Glasses, 1978. Vol. 19, № 5. P. 95—102.
5. Novikov V.K. Development of polymeric model of silicate melts // Rasplavi (Melts), 1987. Vol. 1, № 6. P. 501.
6. Masson C.R., Smith J.B., Whiteway S.G. Activities and ionic distribution in liquid silicates: application of polymer theory // Canad. J. Chem., 1970. 48, P. 1456—1464.
7. Svoistva stekol i stekloobrazujushchikh rasplavov. Spravochnik (Properties of glass and glassforming melts: A Handbook), Mazurin, O.V., etc., Leningrad: Nauka, 1977, Vol. 1.
8. Ebert K., Ederer H. Computeranwendungen in der Chemie. Weinheim: VCH Verlagsgesellschaft mbH, 1985. 416 p.