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**Abstract**

**Full Text**

**PHYSICAL CHEMISTRY**

**S. K. CHUCHMAREV, O. A. ESIN, E. A. PASTUKHOV**

## **ON THE FORM OF EXISTENCE OF TRIVALENT IRON IONS IN MOLTEN SILICATES**

*(Presented by Academician A. N. Frumkin, February 18, 1963)*

Molten silicates may be regarded as a more or less dense packing of comparatively large oxygen anions, part of whose tetrahedral cavities is occupied by network-forming cations (for example, silicon), and part of the octahedral cavities by modifier ions ( $\text{Na}^{2+}$ ,  $\text{Ca}^{2+}$ , etc.). It is considered (<sup>1,2</sup>) that a cation surrounded by a smaller number of oxygen ions (with a noticeable share of covalent bonding) enters into the composition of a complex anion, whereas the modifier cation is "free."

Although trivalent iron, like aluminum, may occur in both forms, the role of each of them has been assessed differently by researchers. Some admit the existence only of the complexes  $\text{FeO}_3^{3-}$  (<sup>3</sup>),  $\text{FeO}_2^-$  and  $\text{Fe}_2\text{O}_4^{2-}$  (<sup>4</sup>), and even  $\text{FeO}^+$  (<sup>5</sup>). On the contrary, others (<sup>6</sup>) suppose the presence only of simple cations  $\text{Fe}^{3+}$ , while still others (<sup>7,8</sup>) consider equilibrium between the two forms possible. We attempted to investigate this question by means of a somewhat modified method of A. N. Frumkin and co-workers (<sup>9,10</sup>), who showed that the maximum contact angle corresponds to the point of zero charge.

**Fig. 1.** Curves  $P_\sigma = f(\varphi)$  at 1350° for a melt of 40% CaO, 40% SiO<sub>2</sub>, 20% Al<sub>2</sub>O<sub>3</sub>.

1 —without addition of Fe<sub>2</sub>O<sub>3</sub>; 2, 3 —with additions of 1.5 and 3.8% Fe<sub>2</sub>O<sub>3</sub>, respectively

A comparatively wide and thick-walled ( $d = 2.5\text{--}4.8$  mm) platinum capillary electrode was anodically polarized in the melt under study at 1350—1520°. Simultaneously, its potential  $\varphi$  was measured (by a commutator with 50 interruptions per second), as was the pressure  $P_\sigma$  required to force a nitrogen bubble out of the capillary.

**Table 1**

**Composition of silicates (in weight %)**

No.	CaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	MeO
1	14.8	18.2	45.5	21.5 Na <sub>2</sub> O
2	33.7	17.6	26.7	21.0 Na <sub>2</sub> O
3	42.2	18.7	17.8	21.3 Na <sub>2</sub> O
4	34.0	16.0	50.0	—
5	15.0	17.0	48.0	20.0—Cs <sub>2</sub> O
6	15.0	17.0	48.0	20.0—SrO

**Table 2**

**Shift of the potential  $\Delta\varphi_m$  upon changing the composition of the melt;**  
 $t^\circ = 1520^\circ$

Silicate No.	Cation	$\frac{z_K}{r_K} \cdot 10^8, \text{ cm}^{-1}$	Fe <sub>2</sub> O <sub>3</sub> , %	$\Delta\varphi_m, \text{ mV}$
4	Ca <sup>2+</sup>	1.88	2.1	+300
6	Sr <sup>2+</sup>	1.57	1.8	+60 (at 1450°)
1	Na <sup>+</sup>	1.02	1.7	+140
5	Cs <sup>+</sup>	0.61	1.7	−90

For the selected diameter and wall thickness of the capillary, the value  $P_\sigma$  depends on wettability and, like the angle  $\theta$ , has a maximum at the potential  $\varphi_m$  corresponding to the point of zero charge. In this connection, the curve  $P_\sigma = f(\varphi)$  has a maximum at the same value of  $\varphi_m$  as  $\theta = f(\varphi)$ , i.e., at the potential corresponding to the point of zero charge.

A shift of  $\varphi_m$  in one direction or another upon addition of small portions of trivalent iron to the melt makes it possible to judge the sign of the charge of the ion predominantly adsorbed at the capillary–electrolyte boundary.

The silicates studied were prepared from chemically pure oxides and had the composition indicated in Table 1.

Part of each of the obtained samples was fused with 10% Fe<sub>2</sub>O<sub>3</sub>, and this ligature was used as an additive that made it possible to obtain different concentrations of trivalent iron. Measurements were carried out in an oxidizing atmosphere (air), which excluded the presence of divalent iron; this was confirmed by chemical analysis of the silicates after the experiments.

The character of the curves  $P_\sigma = f(\varphi)$  is shown in Figs. 1 and 2. In the first of these, the picture is very reminiscent of the arrangement of electrocapillary curves upon addition of a surface-active anion. The value of  $\varphi_m$ , with increasing Fe<sub>2</sub>O<sub>3</sub> content, shifts toward negative values, and it may be considered that trivalent iron is adsorbed as an anion. A different arrangement of the

Fig. 2. Curves  $P_\sigma = f(\varphi)$  at 1520° for silicate No. 3: 1—without addition of  $Fe_2O_3$ , 2-4—with additions of 0.6; 0.9; 1.5%  $Fe_2O_3$ , respectively

Figure 1: Fig. 2. Curves  $P_\sigma = f(\varphi)$  at 1520° for silicate No. 3: 1—without addition of  $Fe_2O_3$ , 2-4—with additions of 0.6; 0.9; 1.5%  $Fe_2O_3$ , respectively

Fig. 3. Effect of the total iron content in the melt on  $\Delta\varphi_m$ : 1-4—silicate No. 1 at 1350, 1400, 1450 and 1520°, respectively; 5-8—silicate No. 2 at 1350, 1400, 1450 and 1520°, respectively; 9-11—silicate No. 3 at 1350, 1400 and 1520°, respectively

Figure 2: Fig. 3. Effect of the total iron content in the melt on  $\Delta\varphi_m$ : 1-4—silicate No. 1 at 1350, 1400, 1450 and 1520°, respectively; 5-8—silicate No. 2 at 1350, 1400, 1450 and 1520°, respectively; 9-11—silicate No. 3 at 1350, 1400 and 1520°, respectively

curves is observed in Fig. 2, as applied to electrolyte No. 3 with a large ratio ( $\%CaO/\%SiO_2$ ). In this case  $\varphi_m$  shifts toward positive potentials, i.e., trivalent iron is adsorbed as a cation.

**Fig. 2.** Curves  $P_\sigma = f(\varphi)$  at 1520° for silicate No. 3: 1—without addition of  $Fe_2O_3$ , 2-4—with additions of 0.6; 0.9; 1.5%  $Fe_2O_3$ , respectively.

**Fig. 3.** Effect of the total iron content in the melt on  $\Delta\varphi_m$ : 1-4—silicate No. 1 at 1350, 1400, 1450 and 1520°, respectively; 5-8—silicate No. 2 at 1350, 1400, 1450 and 1520°, respectively; 9-11—silicate No. 3 at 1350, 1400 and 1520°, respectively.

The dependence of  $\Delta\varphi_m$  on  $Fe_2O_3$  for different temperatures and compositions of the melt is presented in Fig. 3. For the acidic silicate No. 1, for which the ratio

$(\%SiO_2)/(\%CaO) = 3$ , the shift  $\Delta\varphi_m < 0$ , and here adsorption of the anionic form of iron predominates (see curve 1). Apparently, this form is least firmly bound to the given melt and is most readily displaced to the interface. With increasing concentration of  $Fe_2O_3$ , adsorption of the anions first increases and then decreases. It is possible that this is due to an increase both in the content of “free”  $Fe^{3+}$  cations and in their adsorption.

An increase in temperature corresponds to “dissociation” (i.e., to the transition of  $Fe^{3+}$  ions from fourfold to sixfold coordination) of the complex anions and lowers their concentration in the melt. This leads at first to a decrease in anion adsorption (curve 2), and then adsorption of iron cations becomes predominant (curves 3 and 4). A similar increase in adsorption of the cationic form is also observed for other melt compositions (see Fig. 3).

Replacement of part of the network-forming silicon ions by calcium modifier cations, i.e., transition to the more basic silicates Nos. 2 and 3, strengthens the bond of the complex iron anions with the melt. Therefore, it is likely that

here the cationic form is preferentially adsorbed and  $\Delta\varphi_m > 0$  (see curves 5-11). Conversely, if at constant  $\text{SiO}_2$  content 20% CaO is replaced by SrO,  $\text{Na}_2\text{O}$ , and  $\text{Cs}_2\text{O}$ , the potential shift  $\Delta\varphi_m$  becomes less positive, and for  $\text{Cs}_2\text{O}$  even negative (see Table 2).

In other words, when some modifier cations are replaced by others with a lower electrostatic potential ( $z_k/r_k$ ), adsorption of "free"  $\text{Fe}^{3+}$  ions first decreases and then becomes anionic. Apparently, the strength of the bond between the complex iron anions and the melt decreases in this case, which also promotes an increase in their adsorption.

Thus, application of a somewhat modified method of A. N. Frumkin and co-workers makes it possible to confirm experimentally that trivalent iron in liquid silicates is present in at least two coordinations. In this case both forms are capillary-active at the platinum-silicate surface and pass comparatively readily from one into the other when the temperature and composition of the melt are changed.

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