

# Viscosity of Melts of the System $\text{KF—K}_2\text{MoO}_4\text{—SiO}_2$

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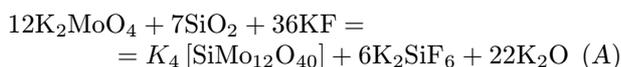
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The viscosity of melts of the system  $\text{KF—K}_2\text{MoO}_4\text{—SiO}_2$  has been measured using the computerized torsional pendulum method. An equation describing the dependence of the viscosity in logarithm values on composition at 1270 K was calculated by multiple linear regression analysis. The sum of viscosities of pure components in logarithm values multiplied by their mole fraction was used as an “additive” behaviour. In the concept of modified Redlich—Kister’s type equation binary and ternary interactions of the particular components were found.

The melts of the system  $\text{KF—K}_2\text{MoO}_4\text{—SiO}_2$  seem to be promising electrolytes for the electrodeposition of molybdenum from fused salts, especially when smooth, adherent molybdenum coatings on metallic surfaces have to be prepared [1, 2]. From the theoretical point of view these melts represent still very little investigated electrolytes containing both the classical ionic components as well as the network-forming ones. The possible chemical interactions between them are not well understood.

Electrolytic molybdenum coating using the electrolytes of the system  $\text{KF—K}_2\text{MoO}_4\text{—SiO}_2$  has been investigated by *Zatko et al.* [1, 2]. From the above system the authors obtained coherent, smooth, and well adhesive molybdenum layers on electrically conductive substrates in a relatively narrow composition region of electrolyte. The quality of the deposit depends on the silica content in the melt. The authors explain the positive role of  $\text{SiO}_2$  in the molybdenum electrodeposition by the change in the structure of the electrolyte and the probable formation of heteropolyanions  $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$  in the melt according to the reaction



Such heteropolyanions are rather voluminous and thus much more polarizable. In the vicinity of the cathode in the electric double layer these anions are strongly polarized and finally disintegrated into smaller species, from which molybdenum deposition takes consecutively place. The X-ray diffraction analysis of the solid deposit on the top closure and furnace wall proved that the deposit consists of pure  $\text{K}_2\text{SiF}_6$ , which supports the assumption on the formation of the above-mentioned heteropolyanions. However, the

authors did not study the mechanism of the cathodic process in this system.

The system  $\text{KF—K}_2\text{MoO}_4\text{—SiO}_2$  is a subsystem of the quinary reciprocal system  $\text{K}^+, \text{Si}^{4+}, \text{Mo}^{6+} // \text{F}^-, \text{O}^{2-}$ , in which a number of compounds may be formed. The phase diagrams of the binary systems  $\text{KF—K}_2\text{MoO}_4$ ,  $\text{KF—SiO}_2$ , and  $\text{K}_2\text{MoO}_4\text{—SiO}_2$ , as well as that of the ternary system  $\text{KF—K}_2\text{MoO}_4\text{—SiO}_2$  in the range up to 50 mole %  $\text{SiO}_2$ , were measured in [3, 4]. In the system  $\text{KF—K}_2\text{MoO}_4$  the intermediate compound  $\text{K}_3\text{FMoO}_4$  is formed with the melting point at 751 °C. The compound divides the system into two simple eutectic ones the coordinates of which are: 29.4 mole %  $\text{K}_2\text{MoO}_4$ , 717.7 °C and 56.9 mole %  $\text{K}_2\text{MoO}_4$ , 747.4 °C. The liquidus curve of  $\text{KF}$  in the binary system  $\text{KF—SiO}_2$  shows an inflex point, characteristic of reciprocal systems with chemical reaction taking place between components. Similar course of the liquidus curve of  $\text{K}_2\text{MoO}_4$  was found also in the binary system  $\text{K}_2\text{MoO}_4\text{—SiO}_2$ , indicating the presence of the chemical reaction between components as well. The strong positive deviation from ideal behaviour of the ternary system  $\text{KF—K}_2\text{MoO}_4\text{—SiO}_2$  was ascribed to the possible formation of heteropolyanions  $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$  in the melt.

In the present work the viscosity of melts of the ternary system  $\text{KF—K}_2\text{MoO}_4\text{—SiO}_2$  was measured using the torsional pendulum method. Based on the obtained results deviation of the viscosity from additive behaviour was calculated in order to get information on interaction of components and possible chemical reaction.

## EXPERIMENTAL

For the preparation of samples the following chemicals were used:  $\text{KF}$  (Lachema),  $\text{K}_2\text{MoO}_4$  and  $\text{SiO}_2$

**Table 1.** Regression Coefficients  $a$ ,  $b$  and the Standard Deviations of Approximation of the Temperature Dependence of the Viscosity (Eqn (1)) of Investigated Melts of the System KF—K<sub>2</sub>MoO<sub>4</sub>—SiO<sub>2</sub>

$x_{\text{KF}}$	$x_{\text{K}_2\text{MoO}_4}$	$x_{\text{SiO}_2}$	$a$	$b/\text{K}$	$\text{SD} \cdot 10^3$	$T$ range/K
1.000	0.000	0.000	-2.374	3014	<0.01	1140—1340
0.750	0.250	0.000	-2.1150	3015	3.01	1060—1200
0.500	0.500	0.000	-1.862	2961	3.72	1070—1210
0.250	0.750	0.000	-1.513	2763	5.47	1100—1220
0.000	1.000	0.000	-1.602	3024	7.87	1220—1340
0.900	0.000	0.100	-3.083	4207	<0.01	1140—1240
0.800	0.000	0.200	-6.157	8855	0.95	1130—1260
0.700	0.000	0.300	-10.950	16155	2.50	1140—1260
0.000	0.900	0.100	-1.750	3168	0.05	1195—1370
0.000	0.800	0.200	-1.790	3247	0.35	1270—1520
0.720	0.180	0.100	-4.088	5759	0.35	1140—1240
0.540	0.360	0.100	-3.018	4510	15.11	1130—1240
0.360	0.540	0.100	-2.419	3778	0.80	1170—1270
0.180	0.720	0.100	-1.957	3365	0.10	1200—1350
0.640	0.160	0.200	-7.598	10700	1.40	1130—1250
0.480	0.320	0.200	-1.594	2985	16.84	1210—1350
0.320	0.480	0.200	-2.371	3950	1.65	1190—1450
0.160	0.640	0.200	-1.778	3233	0.05	1200—1520
0.560	0.140	0.300	-10.682	15616	2.25	1235—1380
0.420	0.280	0.300	-6.849	10434	1.50	1270—1390

Data for the binary system KF—K<sub>2</sub>MoO<sub>4</sub> were taken from [6].

(both Fluka), all anal. grade. KF was dried in the presence of P<sub>2</sub>O<sub>5</sub> at 400 K for one week, then at 430 K under vacuum for one week, K<sub>2</sub>MoO<sub>4</sub> was dried at 680 K for 2 h, and SiO<sub>2</sub> was heated at 1400 K for 2 h. All handling and storage of the chemicals was done in the glove box.

The torsional pendulum method based on the measurement of the logarithmic decrement of damping, caused by the friction in the melt, was used for the viscosity measurement. The measuring device was described in detail in [5].

The measured melts of *ca.* 25 cm<sup>3</sup> in volume were placed in a platinum crucible and were inserted in a resistance furnace. The lid of the furnace was closed and the inert atmosphere was introduced. The platinum cylinder with the diameter of 15 mm and the height of 20 mm was used as the measuring body. The oscillations of the pendulum system were followed by means of two fixed phototransistors, placed in the path of a light beam reflected from a mirror attached to the pendulum. The viscosity values were computed on-line using a Pentium processor. After melting of the sample the pendulum was immersed in the melt, the surface of the melt was kept always 2 mm over the top of the cylinder. The depth of immersion was continuously monitored and controlled using the electrical contact. The additional damping, caused by the cylinder-carrying rod, was eliminated in the computational procedure. The computer has controlled the whole measuring device, including the furnace temperature. After all the input data and the required temperature profile were inserted, the measurement of the viscosity at the desired temperatures was performed automatically. All temperature-dependent

variables (oscillation period in gas, dimensions of the cylinder, damping in gas, density of the measured liquid, moment of inertia of the oscillating system) were expressed in the form of polynomials and calculated for the actual experimental temperature. The experimental error in the viscosity measurement did not exceed 2 %.

The measurements were carried out in the temperature intervals indicated in Table 1. Compounds KF, K<sub>2</sub>MoO<sub>4</sub> and binary KF—K<sub>2</sub>MoO<sub>4</sub> system were measured in the heating mode, others in the cooling mode.

The temperature dependence of the viscosity of the individual melts was described using the equation

$$\ln\{\eta\} = a + \frac{b}{T} \quad (1)$$

where  $\{\eta\}$  is the numerical value of viscosity expressed in mPa s and  $T$  is the temperature in K. The values of the constants  $a$  and  $b$ , obtained by the linear regression analysis, together with the values of the standard deviations of approximation and the measured temperature range for the investigated melts are given in Table 1.

## RESULTS AND DISCUSSION

Several equations for the analysis of the viscosity dependence on the composition can be suggested. One of them arose from the Redlich—Kister's type equation used by *Silný et al.* [6]

$$\eta = \sum_{i=1}^3 x_i \eta_i + \sum_{i \neq j}^3 x_i x_j (A_{ij} + B_{ij} x_j + C_{ij} x_j^2) +$$

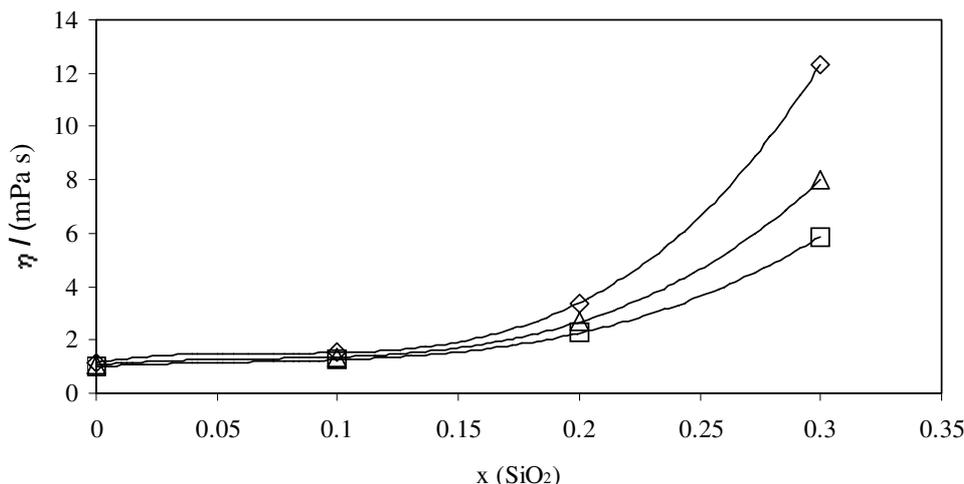


Fig. 1. Viscosity of melts of the binary system KF—SiO<sub>2</sub>.  $\diamond$  1200 K,  $\triangle$  1240 K,  $\square$  1270 K, curves – cubic polynomial functions.

$$+ \sum_{i \neq j \neq k}^3 x_i x_j x_k (A_{ijk} + B_{ijk} x_k) \quad (2)$$

The authors considered that the third term represents interactions of all three components, the second term represents the binary interactions, and the first term should represent ideal behaviour. In the case of transport properties like viscosity the ideal behaviour is not physically defined, since we deal with scalar quantities, which do not possess the total derivative. Thus, the additivity rule cannot be used. On the other hand, this property is thermally activated. Consequently, the additivity of the activation energies can be assumed. Thus, the sum of viscosities of pure components in logarithm values multiplied by their mole fraction can be used as “additive” behaviour. For the description of the viscosity of the three-component system the following equation can be used by *Nguyen and Daněk* [7]

$$\eta = \eta_{id} + \eta_{ex} = \eta_1^{x_1} \eta_2^{x_2} \eta_3^{x_3} + \sum_{i \neq j}^3 x_i x_j \sum_{n=0}^m A_{nij} x_j^n + \sum_{i,j,k}^3 B_{i,j,k} x_i^a x_j^b x_k^c \quad (3)$$

where  $\eta_i$  is viscosity of pure component,  $x_i$  is its mole fraction,  $\eta_{ex}$  is the viscosity excess, and  $a, b, c$  are integers in the range 1–3. One could have some exception about the physical interpretation of eqn (3) thus we suggest its modification in the following form

$$\ln\{\eta\} = \ln\{\eta_{id}\} + \ln\{\eta_{ex}\} = \sum_{i=1}^3 x_i \ln\{\eta_i\} + \sum_{i \neq j}^3 (x_i x_j \sum_{n=0}^m A_{nij} x_j^n) + \sum_{i,j,k}^3 B_{i,j,k} x_i^a x_j^b x_k^c \quad (4)$$

where generally the second and third terms may represent excess viscosity in logarithm values. We con-

sider eqn (4) to be the closest to the physical meaning described above. If we want to use it for a certain temperature, we need to have logarithms of the values of the pure components viscosities at the chosen temperature. Unfortunately, the melting temperature of pure crystalline SiO<sub>2</sub> is far above the temperature used for our experimental investigation. Thus, an extrapolation of the viscosity to 1270 K had to be done for silica glass. The logarithm value of 28.34661 [8, 9] was obtained. It is obvious that in this case it is not possible to determine excess property of the viscosity. The calculation of coefficients  $A$  and  $B$  for the chosen temperature was performed using the multiple linear regression analysis omitting the statistically nonimportant terms on the 0.95 confidence level.

In the above eqn (4) the physical meaning is vanished and some formalism had to be included where a formal viscosity value of pure SiO<sub>2</sub> at given temperature was used likewise in the system KF—K<sub>2</sub>MoO<sub>4</sub>—B<sub>2</sub>O<sub>3</sub> by *Silný et al.* [6]. The viscosity of the subsystem KF—K<sub>2</sub>MoO<sub>4</sub> was discussed in [6].

The viscosity of the binary KF—SiO<sub>2</sub> system at 1200 K, 1240 K, and 1270 K is shown in Fig. 1 and was measured up to 30 mole % SiO<sub>2</sub>. As can be seen, the viscosity increases rapidly with increasing content of SiO<sub>2</sub>. This increase is less pronounced with increasing temperature. The best formal equation describing the dependence of the viscosity on composition at certain temperature can be the cubic polynomial.

The viscosity of the binary K<sub>2</sub>MoO<sub>4</sub>—SiO<sub>2</sub> system at 1200 K, 1240 K, and 1270 K is shown in Fig. 2 and was measured up to 20 mole % SiO<sub>2</sub>. From three points it is difficult to estimate the viscosity behaviour at higher content of SiO<sub>2</sub>. Nevertheless, in the measured region the viscosity can be described by quadratic function of mole fraction of SiO<sub>2</sub> with very low minimum at 10 mole % SiO<sub>2</sub>.

The final formal equation of the logarithm viscosity at 1270 K of the ternary system KF—K<sub>2</sub>MoO<sub>4</sub>—SiO<sub>2</sub>

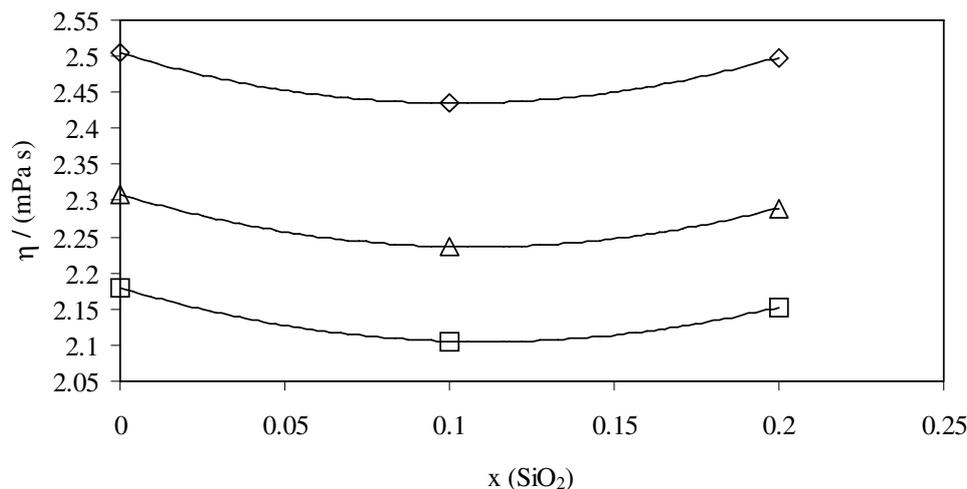


Fig. 2. Viscosity of melts of the binary system K<sub>2</sub>MoO<sub>4</sub>—SiO<sub>2</sub>.  $\diamond$  1200 K,  $\triangle$  1240 K,  $\square$  1270 K, curves – quadratic polynomial functions.

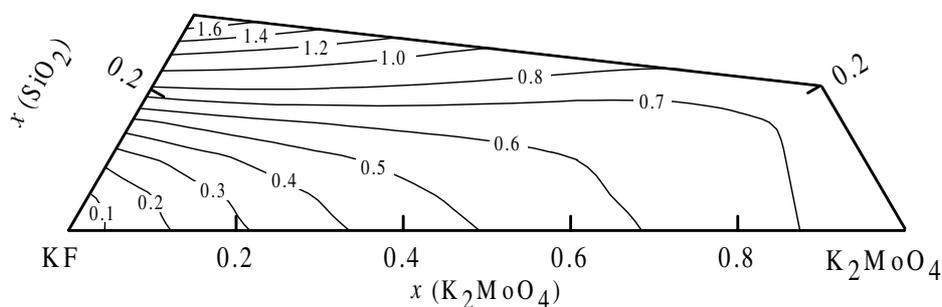


Fig. 3. Viscosity of melts of the ternary system KF—K<sub>2</sub>MoO<sub>4</sub>—SiO<sub>2</sub> at 1270 K. Values are expressed in logarithm scale.

was obtained in the following form

$$\begin{aligned} \ln\{\eta\} = & 0.03944x_{\text{KF}} + 0.7811x_{\text{K}_2\text{MoO}_4} + 28.35x_{\text{SiO}_2} - \\ & - 4.131x_{\text{KF}}^2x_{\text{SiO}_2}^2 - 6.193x_{\text{K}_2\text{MoO}_4}^2x_{\text{SiO}_2}^2 + \\ & + 0.7527x_{\text{KF}}^2x_{\text{K}_2\text{MoO}_4} - 27.84x_{\text{KF}}^2x_{\text{SiO}_2} - \\ & - 27.42x_{\text{K}_2\text{MoO}_4}^2x_{\text{SiO}_2} - 79.75x_{\text{KF}}x_{\text{K}_2\text{MoO}_4}x_{\text{SiO}_2}^2 - \\ & - 54.26x_{\text{KF}}x_{\text{K}_2\text{MoO}_4}^2x_{\text{SiO}_2} - 50.13x_{\text{KF}}^2x_{\text{K}_2\text{MoO}_4}x_{\text{SiO}_2} \end{aligned} \quad (5)$$

The standard deviation of the fit in logarithm value is 0.00703 mPa s. This temperature was chosen because it was starting measuring temperature of the binary K<sub>2</sub>MoO<sub>4</sub>—20 mole % SiO<sub>2</sub> system. This temperature is significantly higher than the temperature of primary crystallization from phase diagram [4], but due to the very long time needed for the dissolution of SiO<sub>2</sub> it was necessary to start the measurement at higher temperature. The viscosities of the mixtures that were measured at lower maximum temperatures can be easily calculated from almost perfectly linear dependences of  $\ln\{\eta\}$  vs.  $1/T$ . The opposite process is impossible to perform, because when the crystalline solid state is reached by cooling the viscosity changes to extremely high values. The viscosity of the ternary system is shown in Fig. 3.

Here we can expand the discussion of physical meaning of the coefficients *A* and *B*. They represent

logarithm values of certain contribution to the overall viscosity (in logarithm value). This contribution can arise from binary interactions or ternary interactions. It is a certain mathematical correction to describe a certain hypersurface of measured viscosity (in logarithm values). Generally, it may be connected to the conception of the excess viscosity but in this concrete system it should be better to consider it as a mathematical correction because of very rough extrapolation of SiO<sub>2</sub> viscosity.

The above discussion does not exclude the assumption that some interactions of KF with SiO<sub>2</sub>, KF with K<sub>2</sub>MoO<sub>4</sub>, and K<sub>2</sub>MoO<sub>4</sub> with SiO<sub>2</sub> are expected together with ternary interactions. The result of these interactions can be the formation of some compounds present in the melt. Thus, according to the reaction (A) the formation of suggested heteropolyanions [SiMo<sub>12</sub>O<sub>40</sub>]<sup>4-</sup> and [SiF<sub>6</sub>]<sup>2-</sup> seems to be reasonable. This conclusion of course must be proved by some other techniques, e.g. by neutron diffraction experiments in the melt.

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