Surface Tension of Melts of the System KF—K$_2$MoO$_4$—SiO$_2$

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The surface tension of the molten system KF—K$_2$MoO$_4$—SiO$_2$ has been determined using the maximum bubble pressure method. The error in the surface tension measurement was estimated to be ± 1 %. On the basis of the obtained data the concentration dependence of the surface tension and of the surface tension excess of the investigated system was calculated. The results are discussed in terms of the anionic composition.

The melts of the system KF—K$_2$MoO$_4$—SiO$_2$ seem to be promising electrolytes for the electrodeposition of molybdenum from fused salts, especially when smooth, adherent molybdenum coating on metallic surfaces has to be prepared [1, 2]. From the theoretical point of view these melts represent very little investigated electrolytes containing both the classical ionic components and the network-forming one. The possible chemical interactions between them are not well understood. The knowledge of the structure of these melts is needed for the understanding of the mechanism of the electrochemical process involving electrodeposition of molybdenum on the electrode surface. The interaction of components and the possible reactions, which may take place in the melt, affect the ionic composition, thus affecting the kind of the electroactive species.

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

$$12K_2MoO_4 + 7SiO_2 + 36KF =$$
$$= K_4\left[SiMo_{12}O_{40}\right] + 6K_2SiF_6 + 22K_2O \quad (A)$$
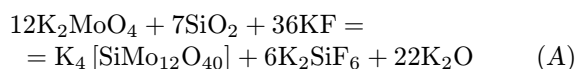
Such heteropolyanions are rather voluminous and thus much more polarizable. In the vicinity of the cathode in the electric double layer this anion is strongly polarized and finally disintegrated into smaller species, from which consecutive molybdenum deposition takes place. The X-ray diffraction analysis of the solid deposit on the top closure and furnace wall proved that the deposit consists of pure K$_2$SiF$_6$, which supports the taking place of the above reaction. However, the authors did not study the mechanism of the cathodic process in this system.

The system is a subsystem of the quinary reciprocal system K$^+$, Si^{4+}, Mo^{6+} // F$^-$, O^{2-}, in which a number of compounds may form. No literature data can be found on physicochemical properties of the ternary system KF—K$_2$MoO$_4$—SiO$_2$. Only the phase diagrams of the binary subsystems and whole system are known and discussed in detail [3].

The surface tension reflects the nature of chemical bonds between species of the system being investigated. Due to the different coulombic interaction between species in the melt, the anions being more covalent in character are concentrated on the surface and become surface-active. Therefore the anionic composition, and in the case of the system KF—K$_2$MoO$_4$—SiO$_2$ especially the content of SiO$_2$, forming probably the strongest covalent species, will influence substantially the concentration dependence of the surface tension of these melts.

In the present work, the surface tension of the KF—K$_2$MoO$_4$—SiO$_2$ melts has been measured using the maximum bubble pressure method. Based on the obtained data the concentration dependence of the surface tension and of the surface tension excess of the investigated system was calculated. The results are discussed in terms of the anionic composition.

EXPERIMENTAL

For the preparation of samples the following chemicals were used: KF (Lachema), K$_2$MoO$_4$ and SiO$_2$ (both Fluka), all anal. grade. KF was dried in vacuum in the presence of P$_2$O$_5$ for two weeks and then at 453 K in vacuum without P$_2$O$_5$, K$_2$MoO$_4$ was dried at 680 K for 2 h, and SiO$_2$ was preheated and crushed

in an agate mortar. All handling and storage of the chemicals was done in the glove box.

The measuring device consisted of a resistance furnace provided with an adjustable head fixing the position of the capillary (PtRh20), the Pt—PtRh10 thermocouple, and a platinum wire, which served as electric contact to adjust the exact touch of the capillary with the liquid surface.

The temperature controller PRT-K was used to adjust the needed operational constants for the temperature control of the furnace using an additional Pt—PtRh10 control thermocouple placed in between the working and heating shafts of the furnace. The voltmeter MT-100 was used for temperature measurement.

The capillary (PtRh20) with an outer diameter of 3 mm was used. In order to obtain precise results, the capillary tip was carefully machined. The orifice had to be as circular as possible, with a sharp conical edge. An angle of capillary tip and capillary centre line was approximately 45 degrees. A precise inner diameter of the capillary is very important if accurate measurements are to be performed. The metallographic microscope Jenapol was used to measure the diameter of the orifice, which was 1.087 mm. The actual capillary radius at a given temperature was calculated using the thermal expansion data for platinum.

A special water-cooled furnace lid was used for the capillary support. A micrometric screw, fixed on the lid, determined the position for the exact touch of the capillary with the liquid surface and indicated the desired immersion depth with an accuracy of 0.01 mm.

The digital micromanometer COMMET LB/ST 1000 with two measuring ranges, 200 Pa and 1000 Pa, was used for pressure determination. This enabled us to measure the pressure with an accuracy of ± 1 Pa. Nitrogen was used to form the bubbles and to maintain an inert atmosphere over the sample. The nitrogen purity was 99.99 % and before reaching the apparatus it was dried bubbling through the concentrated sulfuric acid. The gas was slowly fed through the capillary during the experiment to avoid condensation in the upper part of capillary. The nitrogen flow was adjusted using a fine needle valve. The rate of bubble formation was approximately 1 bubble in 20—30 s.

The surface tension may be calculated according to the equation [4]

$$\sigma = \frac{r}{2}\left(P_{\max} - ghd\right) \qquad (1)$$

where r is the capillary radius, $P_{\max}$ is the maximum bubble pressure when the bubble is a hemisphere with the radius equal to the radius of the capillary, g is the gravitational constant, h is the depth of immersion of the capillary, and d is the density of the melt. However, there is also the possibility to calculate the surface tension of the liquid without knowing the density of

the melt. Eliminating the density, d, from eqn (1) for two different immersion depths we obtain the equation

$$\sigma = \frac{r}{2}\,\frac{P_{\max,1} \cdot h_2 - P_{\max,2} \cdot h_1}{h_2 - h_1} \qquad (2)$$

where $P_{\max,i}$ is the maximum bubble pressure at immersion depth h_i. Although the density data for the investigated melts were known, eqn (2) was preferably used for the investigated melts.

The surface tension of each sample was measured at 5—7 different temperatures in the range of 80—100 K starting approximately 20 K above the temperature of primary crystallization (T_{m}). The surface tension measurements were carried out at four different depths of immersion (usually 2.00 mm, 3.00 mm, 4.00 mm, and 5.00 mm) yielding six surface tension values for each temperature.

In the ternary system KF—K$_2$MoO$_4$—SiO$_2$ cross-sections with the constant mole ratio $x(\mathrm{KF})/x(\mathrm{K_2MoO_4}) = 0.333, 1$, and 3 were chosen for the measurement. In the boundary binary systems and in the above-mentioned cross-sections the figurative points with the content of 10 mole %, 20 mole %, and 30 mole % SiO$_2$ were selected.

In the surface tension measurements using the maximum bubble pressure method several sources of error may occur. As mentioned above, the exact machining of the capillary orifice is important. A deviation from a circular orifice caused in our case an error of ± 0.3 %. The determination of the immersion depth with an accuracy of ± 0.01 mm introduced an error of ± 0.3 %. The accuracy of ± 1 Pa in the pressure measurement caused an additional error of ± 0.4 %. The sum of all these errors gives an estimated total error of approximately ± 1 %. The standard deviations of the experimental data based on the least-squares statistical analysis were in the range (0.5—1.8) mN m^{-1}, which corresponds to the estimated error.

The experimental set up was checked by measuring the surface tension of pure molten sodium chloride. The obtained data agreed within the estimated error with those given by *Janz* [5, 6].

The temperature dependence of the surface tension was expressed by the linear equation

$$\sigma = a - bt \qquad (3)$$

where σ is the surface tension in mN m^{-1} and t is the temperature in °C. The values of constants a and b in eqn (3), obtained using the linear regression analysis, together with the values of the standard deviations of approximation for the investigated KF—K$_2$MoO$_4$—SiO$_2$ melts are given in Table 1. The surface tension of SiO$_2$ was taken from [7].

Table 1. Coefficients a and b of the Temperature Dependence of the Surface Tension and the Standard Deviations of Approximation (sd) of Individual Melts of the System KF—K_2MoO_4—SiO_2

x_{KF}	$x_{K_2MoO_4}$	x_{SiO_2}	$\dfrac{a}{\text{mN m}^{-1}}$	$\dfrac{b}{\text{mN m}^{-1}\ ^\circ\text{C}^{-1}}$	$\dfrac{\text{sd}}{\text{mN m}^{-1}}$	$\dfrac{T\ \text{range}}{^\circ\text{C}}$
1.00	0	0	240.03	0.08478	0.35	$\langle 910$—$980\rangle$
0.90	0	0.10	222.12	0.08720	0.81	$\langle 920$—$980\rangle$
0.80	0	0.20	275.65	0.14458	1.14	$\langle 930$—$990\rangle$
0.70	0	0.30	299.40	0.17031	0.58	$\langle 940$—$1000\rangle$
0	1.00	0	210.73	0.08130	1.71	$\langle 940$—$1000\rangle$
0	0.90	0.10	320.38	0.18145	0.66	$\langle 950$—$1020\rangle$
0	0.80	0.20	482.48	0.36360	1.83	$\langle 1050$—$1100\rangle$
0	0	1.00	251.7	-0.0310	6.0	$\langle 1500$—$1800\rangle$
0.80	0.20	0	202.33	0.06558	0.70	$\langle 860$—$940\rangle$
0.60	0.40	0	201.45	0.06747	0.62	$\langle 770$—$910\rangle$
0.50	0.50	0	206.07	0.07451	0.94	$\langle 770$—$910\rangle$
0.40	0.60	0	205.90	0.07380	0.85	$\langle 790$—$920\rangle$
0.20	0.80	0	208.80	0.07877	0.85	$\langle 870$—$960\rangle$
0.56	0.14	0.30	306.32	0.15135	1.14	$\langle 1090$—$1130\rangle$
0.42	0.28	0.30	243.62	0.09955	0.83	$\langle 1090$—$1150\rangle$
0.64	0.16	0.20	240.96	0.09290	0.95	$\langle 1110$—$1150\rangle$
0.48	0.32	0.20	261.49	0.11130	0.88	$\langle 1090$—$1140\rangle$
0.32	0.48	0.20	281.03	0.12792	1.06	$\langle 1090$—$1150\rangle$
0.16	0.64	0.20	152.36	0.01109	2.27	$\langle 1090$—$1150\rangle$
0.72	0.18	0.10	218.82	0.08130	0.99	$\langle 940$—$1000\rangle$
0.54	0.36	0.10	236.92	0.09907	0.51	$\langle 960$—$1010\rangle$
0.36	0.54	0.10	170.87	0.03117	1.40	$\langle 1000$—$1060\rangle$
0.18	0.72	0.10	271.47	0.11944	0.63	$\langle 1000$—$1060\rangle$

RESULTS AND DISCUSSION

The surface tension of the boundary binary systems KF—K_2MoO_4, KF—SiO_2, and K_2MoO_4—SiO_2 at the temperatures $827\,^\circ$C, $877\,^\circ$C, and $927\,^\circ$C is shown in Figs. 1—3, respectively.

To get some information on the structure of the melt it is very important to define the course of the surface tension in ideal solutions. A general approach used for the variation of surface tension with composition was given by *Guggenheim* [8], who stated that the surface tension of an ideal solution should follow the simple additivity formula to a good approximation. To describe the excess surface tension in the real system *e.g.* the Redlich—Kister's type excess function can be used. For the surface tension of the real ternary system it can then be written

$$\sigma = \sum_{i=1}^{3} \sigma_i x_i + \sum_{\substack{i=1 \\ i\neq j}}^{3} \left(x_i x_j \sum_{n=0}^{k} A_{nij} x_j^n \right) +$$
$$+ x_1 x_2 x_3 \sum_{m=1}^{l} B_m x_1^a x_2^b x_3^c \qquad (4)$$

In eqn (4) σ_i's are the surface tensions of pure components and x_i's are their mole fractions in the mixture. Exponents a, b, c are integers in the range 0—2. The first term represents the ideal behaviour, the second one the interactions in the binary systems, and the third one the interactions of all three components.
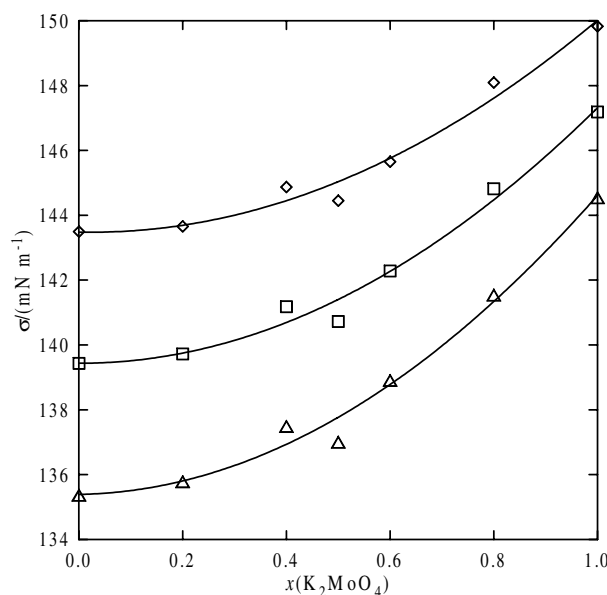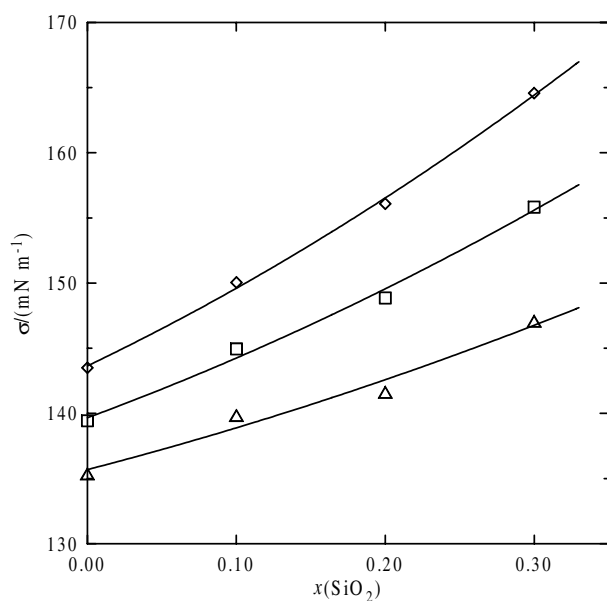

Fig. 1. Surface tension in the system KF—K_2MoO_4. $\Diamond$ $827\,^\circ$C, $\square$ $877\,^\circ$C, $\triangle$ $927\,^\circ$C, solid lines – calculated according to quadratic equation.

The calculation of the coefficients A_{nij} and B_m for the system KF(1)—K_2MoO_4(2)—SiO_2(3) was performed using the multiple linear regression analysis, omitting the statistically unimportant terms on the 0.99 confidence level. The following final equation was obtained
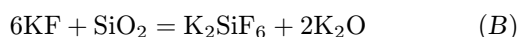
Table 2. Coefficients σ_i and A_{nij} of the Concentration Dependence of Surface Tension of the System KF(1)—K$_2$MoO$_4$(2)—SiO$_2$(3) and the Standard Deviations of Approximation, sd, at Individual Temperatures

Coefficient	Temperature		
	827 °C	877 °C	927 °C
$\sigma_1/(\text{mN m}^{-1})$	142.2 ± 1.6	138.6 ± 1.4	135.1 ± 1.4
$\sigma_2/(\text{mN m}^{-1})$	150.4 ± 1.6	146.2 ± 1.4	142.0 ± 1.4
$\sigma_3/(\text{mN m}^{-1})$	277.9 ± 4.3	278.9 ± 3.8	279.7 ± 4.0
$A_{013}/(\text{mN m}^{-1})$	−93.65 ± 12.54	−116.7 ± 10.5	−140.0 ± 10.7
$A_{123}/(\text{mN m}^{-1})$	1059.3 ± 88.2	854.1 ± 73.4	649.7 ± 74.2
sd$/(\text{mN m}^{-1})$	3.6	3.0	3.1

Fig. 2. Surface tension in the system KF—SiO$_2$. ◇ 827 °C, □ 877 °C, △ 927 °C, solid lines – calculated according to quadratic equation.

Fig. 3. Surface tension in the system K$_2$MoO$_4$—SiO$_2$. ◇ 827 °C, □ 877 °C, △ 927 °C, solid lines – calculated according to quadratic equation.
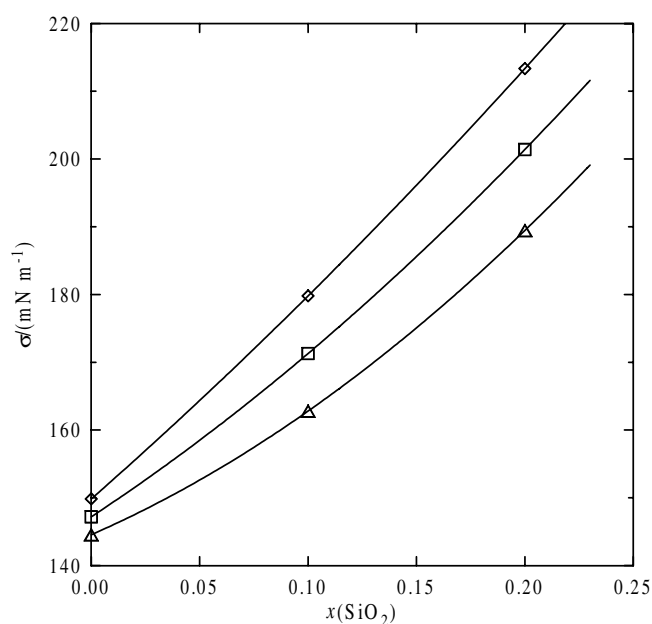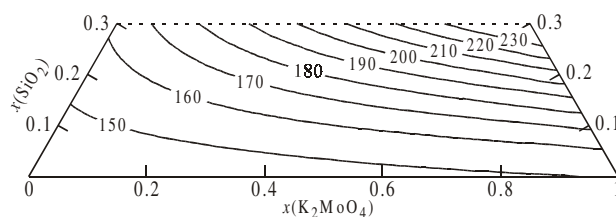
$$\sigma = \sigma_1 x_1 + \sigma_2 x_2 + \sigma_3 x_3 + A_{013} x_1 x_3 + A_{123} x_2 x_3^2 \quad (5)$$

The calculated values of the surface tension of pure components, σ_i, the coefficients A_{nij}, and the standard deviations of approximation for the chosen temperatures of 827 °C, 877 °C, and 927 °C are given in Table 2. Statistically important interactions were found only in the binary system KF—SiO$_2$ and in the ternary system KF—K$_2$MoO$_4$—SiO$_2$. It means that the interaction in the binary system KF—K$_2$MoO$_4$ leading to the formation of the congruently melting compound K$_3$FMoO$_4$ is statistically unimportant compared with those in the binary and the ternary systems. The interaction in the binary system KF—SiO$_2$ can be attributed to the formation of K$_2$SiF$_6$ according to the reaction in liquid state

$$6KF + SiO_2 = K_2SiF_6 + 2K_2O \qquad (B)$$
$$\Delta_r G^{\circ}_{827\,°C} = 657.5 \text{ kJ mol}^{-1} \qquad (6)$$

Even when the reaction Gibbs energy, of reaction (B),

Fig. 4. Surface tension of the system KF—K$_2$MoO$_4$—SiO$_2$ at the temperature of 827 °C. Values are $\sigma/(\text{mN m}^{-1})$.

has a positive value, the reaction can take place because the formed K$_2$O is removed from the melt due to the reactions with other components of the melt. It should be noted that in the calculation the formation Gibbs energy of K$_2$SiF$_6$ was estimated from formation Gibbs energies of KF and SiF$_4$ at given temperature. The interaction in the ternary system can be explained by the formation of the heteropolyanions [SiMo$_{12}$O$_{40}$]$^{4-}$ according to the reaction (A). How-
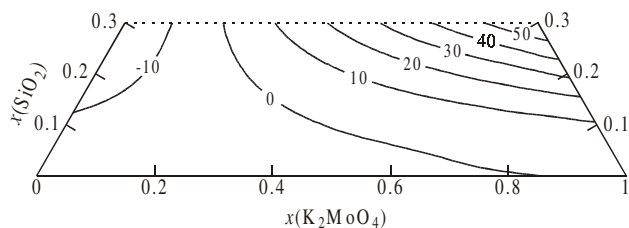
Fig. 5. Surface tension excess in the system KF—K$_2$MoO$_4$—SiO$_2$ at the temperature of 827 °C. Values are $\sigma/$(mN m^{-1}).

ever, the thermodynamic probability of this reaction could not be proved due to the lack of thermodynamic data.

The surface tension and surface tension excess of the ternary system at 827 °C are shown in Figs. 4 and 5.

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