Surface Tension of Melts of the System $KF—K_2MoO_4—B_2O_3$

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The surface tension of the molten system $KF—K_2MoO_4—B_2O_3$ 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 composition dependence of the surface tension and of the surface tension excess of the investigated system was calculated and compared with the results of other previously determined physicochemical properties. The results are discussed in terms of the anionic composition.

The melts of the system $KF—K_2MoO_4—B_2O_3$ 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 boron and the synthesis of titanium diboride on the electrode surface. The interaction of components and the possible reactions which may take place in the melt influence the ionic composition, thus affecting the kind of the electroactive species.

The system $KF—K_2MoO_4—B_2O_3$ is a considerably complicated subsystem of the quinary reciprocal system K^+, B^{3+}, Mo^{6+} // F^-, O^{2-}, in which a number of compounds is formed. The phase diagram of the system $KF—K_2MoO_4—B_2O_3$ was determined in [3]. In the system $KF—K_2MoO_4—B_2O_3$ the intermediate compound K_3FMoO_4, melting congruently at 751 °C, is formed. This compound divides the binary system $KF—K_2MoO_4$ into two simple eutectic ones the coordinates of which are: 29.4 mole % K_2MoO_4, t_e = 717.7 °C and 56.9 mole % K_2MoO_4, t_e = 747.4 °C. In the binary system $KF—B_2O_3$ the liquidus curve decreases monotonically with increasing content of B_2O_3. The inflection point was found in the course of the liquidus curve of K_2MoO_4 in the binary system $K_2MoO_4—B_2O_3$. The strong positive deviation from ideal behaviour was ascribed to the possible formation of heteropolyanions $[BMo_6O_{24}]^{9-}$ in the melt. In the investigated composition range of the ternary system one eutectic point has been found the coordinates of which are: 57 mole % KF, 24 mole % K_2MoO_4, 19 mole % B_2O_3, and t_e = 682 °C. The standard deviation of approximation in the calculated ternary phase diagram is ± 5.2 °C. The volume properties and the viscosity of the ternary system $KF—K_2MoO_4—B_2O_3$ up to 30 mole % B_2O_3 have been published in our previous works [4, 5].

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 $KF—K_2MoO_4—B_2O_3$ melts, the anions being more covalent in character are concentrated on the surface and become surface-active. Therefore the anionic composition, especially the content of B_2O_3, forming the strongest covalent species, will substantially influence the composition dependence of the surface tension of these melts.

In the present work the surface tension of the $KF—K_2MoO_4—B_2O_3$ melts has been measured using the maximum bubble pressure method. The surface tension of this system could not be found in the literature so far. On the basis of the obtained data the composition dependence of the surface tension and of the surface tension excess of the investigated system was calculated and compared with the results of other previously determined physicochemical properties. The results are discussed in terms of the anionic composition.

EXPERIMENTAL

For the preparation of samples the following chemicals were used: KF (Lachema), K_2MoO_4 and B_2O_3 (both Fluka), all anal. grade. KF was dried in vac-

uum at 400 K in the presence of P_2O_5 for two weeks, K_2MoO_4 was dried at 680 K for 2 h, and B_2O_3 was remelted and crushed in an agate mortar. All handling and storage of the chemicals was done in a glove box.

The measuring device consisted of a resistance furnace provided with an adjustable head fixing the position of the platinum capillary, 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.

A 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. A voltmeter MT-100 was used for temperature measurement.

A platinum capillary 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. The precise inner diameter of the capillary is very important if accurate measurements are to be performed. A metallographic microscope JENAPOL was used to measure the diameter of the orifice. The orifice diameter 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 indicating the desired immersion depth with an accuracy of 0.01 mm.

A digital micromanometer COMMET LB/ST 1000 with two measuring ranges, 200 Pa and 1000 Pa, was used for pressure determination. This enabled 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 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

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

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 acceleration due to gravity, h is the depth of immersion of the capillary, and d is the density of the melt [6]. 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 results in the equation

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

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 value T_m of the measured sample was taken from the previous phase diagram measurements [3]. 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_2MoO_4—B_2O_3 cross-sections with the constant mole ratio $x(KF)/x(K_2MoO_4)$ = 0.333, 1, and 3, were chosen for the measurement. In the boundary binary systems and in the aforementioned cross-sections the figurative points with the content of 10 mole %, 20 mole %, and 30 mole % B_2O_3 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 approx. ± 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 comparison of the obtained data with those given by *Janz et al.* [7, 8] agreed within the estimated error.

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_2MoO_4—B_2O_3 melts are given in Table 1. The temperature dependence of the surface tension of B_2O_3 was taken from [9].

Table 1. Coefficients a and b of the Temperature Dependence of the Surface Tension and the Standard Deviations (SD) of Approximation of Individual Melts of the System KF—K_2MoO_4—B_2O_3

x_{KF}	$x_{K_2MoO_4}$	$x_{B_2O_3}$	a	b	SD
			mN m^{-1}	mN m^{-1} °C^{-1}	mN m^{-1}
1	0	0	193.59	0.05291	0.82
0.90	0	0.10	258.73	0.15034	0.68
0.80	0	0.20	239.65	0.12966	0.53
0.70	0	0.30	241.85	0.12967	0.77
0	1	0	210.73	0.08130	1.71
0	0.90	0.10	212.05	0.08631	0.80
0	0.80	0.20	220.80	0.09844	0.94
0	0.70	0.30	224.56	0.10542	0.83
0.80	0.20	0	202.33	0.06558	0.70
0.60	0.40	0	201.45	0.06747	0.62
0.50	0.50	0	206.07	0.07451	0.94
0.40	0.60	0	205.90	0.07380	0.85
0.20	0.80	0	208.80	0.07877	0.85
0.175	0.525	0.30	254.78	0.13290	0.58
0.35	0.35	0.30	236.71	0.11709	0.61
0.525	0.175	0.30	252.99	0.14278	1.83
0.20	0.60	0.20	241.08	0.12305	1.42
0.40	0.40	0.20	245.19	0.127321	0.55
0.60	0.20	0.20	228.77	0.11319	1.80
0.225	0.675	0.10	242.82	0.11688	0.49
0.45	0.45	0.10	265.81	0.15336	0.96
0.675	0.225	0.10	251.60	0.14314	1.76

RESULTS AND DISCUSSION

To get some information on the structure of the melt it is very important to define the course of the surface tension in the ideal solution. A general approach used for the variation of surface tension with composition was given by *Guggenheim* [10], 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. Then for the surface tension of the real ternary system it can 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) the values σ_i are the surface tensions of pure components and the values x_i are their mole fractions in the mixture. Coefficients a, b, c, and n 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.

The calculation of the coefficients A_{nij} and B_m for the system KF(1)—K_2MoO_4(2)—B_2O_3(3) was performed using the multiple linear regression analysis, omitting the statistically nonimportant terms on the 0.99 confidence level. The following final equation was obtained

$$\sigma = \sigma_1 x_1 + \sigma_2 x_2 + \sigma_3 x_3 + x_1 x_3 (A_{013} + A_{113} x_3) + x_2 x_3 (A_{123} x_2 + A_{223} x_2^2) \qquad (5)$$

The values of the surface tension of pure components, σ_i, coefficients A_{nij} and B_m, and the standard deviations of approximation for the chosen temperatures of 1100 K, 1150 K, and 1200 K are given in Table 2.

The surface tension of the boundary binary systems KF—K_2MoO_4, KF—B_2O_3, and K_2MoO_4—B_2O_3 at the temperatures 1100 K, 1150 K, and 1200 K is shown in Figs. 1—3, respectively.

No binary interaction was found in the system KF—K_2MoO_4 obviously due to the almost ideal behaviour, as it was evidenced by the thermodynamic analysis [3] and volume properties [4]. In the system KF—K_2MoO_4 the surface tension increases surprisingly with increasing content of K_2MoO_4 (Fig. 1). One would expect that due to the covalent Mo—O bonds K_2MoO_4 is the surface-active component. However, the MoO_4^{2-} anions are obviously strongly solvated by the fluoride ones not allowing them to concentrate on the surface. This explanation supports also the negative surface adsorption of K_2MoO_4 calculated in [11].

For a system in chemical equilibrium at constant pressure the Gibbs equation for the surface tension is valid [12]

$$\mathrm{d}\sigma = -S^s \,\mathrm{d}T - \sum_i \Gamma_i \mathrm{d}\mu_i \qquad (6)$$

where σ is the surface tension, S^s is the surface entropy, Γ_i is the relative surface adsorption, and μ_i

Table 2. Coefficients σ_i, A_{nij} of the Composition Dependence of the Surface Tension of the System KF(1)—K_2MoQ_4(2)—B_2O_3(3) and the Standard Deviations of Approximation, SD, at Individual Temperatures

Coefficient	Temperature		
mN m^{-1}	1100 K	1150 K	1200 K
σ_1	142.37 ± 1.27	138.11 ± 1.58	133.84 ± 2.04
σ_2	148.81 ± 1.21	145.39 ± 1.50	141.93 ± 1.94
σ_3	80.37 ± 1.04	78.61 ± 1.29	76.84 ± 1.68
A_{013}	−83.62 ± 22.06	−128.53 ± 26.92	−173.46 ± 34.26
A_{113}	457.16 ± 75.20	561.59 ± 91.30	666.10 ± 115.58
A_{123}	366.44 ± 46.00	299.88 ± 56.21	232.73 ± 71.63
A_{223}	−423.49 ± 62.45	−357.75 ± 76.31	−290.79 ± 97.25
SD	1.74	2.13	2.72

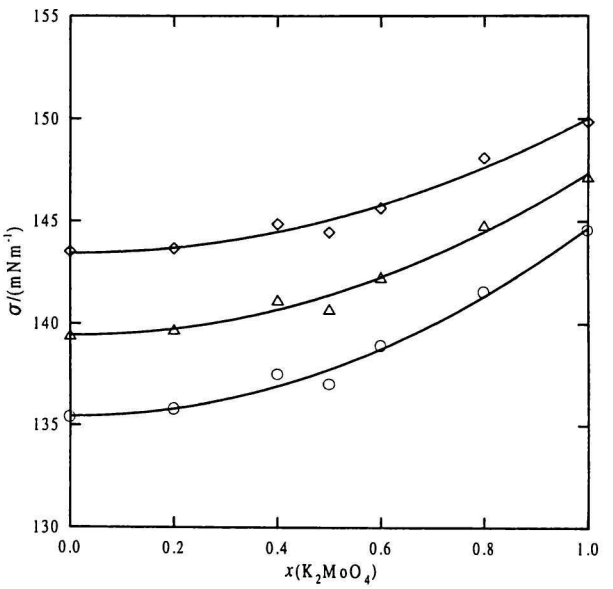

Fig. 1. Surface tension in the system KF—K_2MoO_4. ◇ 1100 K, △ 1150 K, ○ 1200 K, solid lines – calculated according to eqn (*5*).

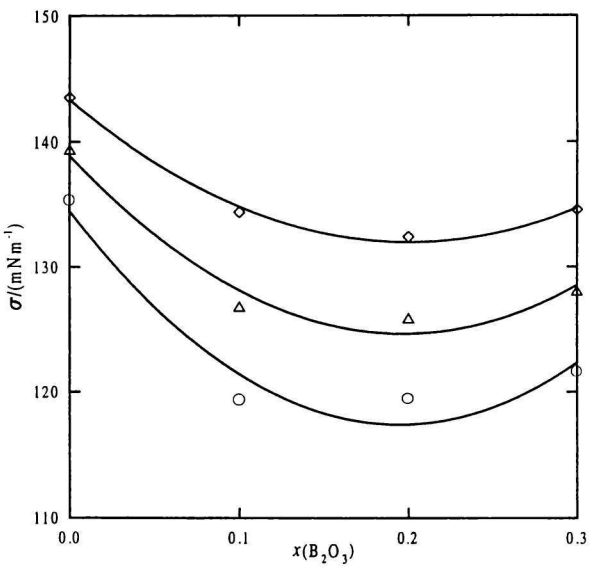

Fig. 2. Surface tension in the system KF—B_2O_3. ◇ 1100 K, △ 1150 K, ○ 1200 K, solid lines – calculated according to eqn (*5*).

is the chemical potential of component i. The Gibbs equation enables to calculate the surface entropy, S^s, from the temperature dependence of the surface tension

$$S^s = -\left[\frac{d\sigma}{dT}\right]_{\mu_i} \qquad (7)$$

The surface entropy is related to the structure and the distribution of species on the surface. Hence this property will also be related to the distribution of ions in the bulk due to equilibrium between surface and bulk. There is, however, no simple relation between the composition of the surface and the bulk due to the preference for species with covalent character to concentrate on the surface.

Comparing eqns (*3*) and (*7*) it is obvious that the surface entropy is equal to the coefficient b in eqn (*3*). In Fig. 6 the plot of the surface entropy *vs.* mole fraction for the boundary binary system KF—K_2MoO_4 is shown. The surface entropy increases monotonically with increasing content of K_2MoO_4, which reflects the increasing complexity of the melts in comparison with the relative simple structure of the pure KF melt.

In the system KF—B_2O_3 the surface tension decreases with increasing content of B_2O_3 (Fig. 2). According to the results of the KF liquidus curve analysis in this system performed by *Chrenková* and *Daněk* [13] the following reaction takes place in this system

$$8KF + 7B_2O_3 = 3K_2B_4O_7 + 2KBF_4 \qquad (A)$$

The presence of the surface-active compounds $K_2B_4O_7$ and KBF_4 having covalent bonds obviously lowers the surface tension of KF and their formation in this system is evidenced also by the significant binary interaction in this system.

Also in the system K_2MoO_4—B_2O_3 the surface tension decreases with increasing content of B_2O_3

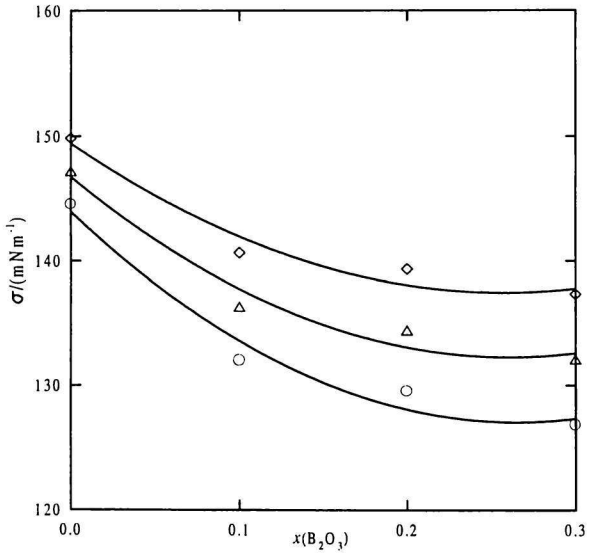

Fig. 3. Surface tension in the system K_2MoO_4—B_2O_3. ◊ 1100 K, Δ 1150 K, o 1200 K, solid lines – calculated according to eqn (*5*).

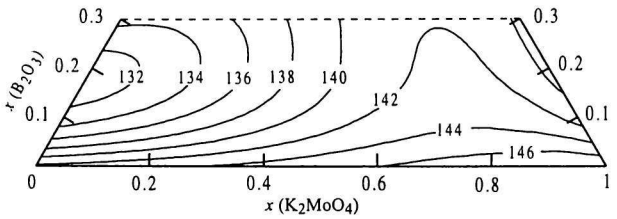

Fig. 4. Surface tension in the system KF—K_2MoO_4—B_2O_3 at the temperature of 1100 K. Values are $\sigma/(\mathrm{mN\ m^{-1}})$.

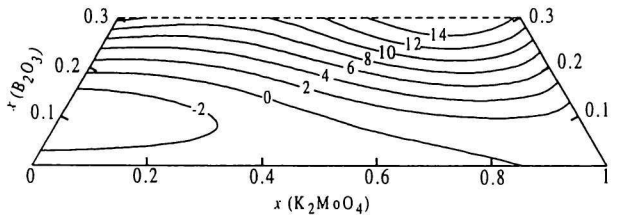

Fig. 5. Surface tension excess in the system KF—K_2MoO_4—B_2O_3 at the temperature of 1100 K. Values are $\sigma/(\mathrm{mN\ m^{-1}})$.

(Fig. 3). In [14] the formation of heteropolyanions according to the reaction

$$6K_2MoO_4 + 2B_2O_3 = K_9[BMo_6O_{24}] + 3KBO_2 \quad (B)$$

was suggested. These heteropolyanions, as well as the originated borate anions may be surface-active with respect to the pure K_2MoO_4 due to the presence of covalent Mo—O and B—O bonds thus lowering the

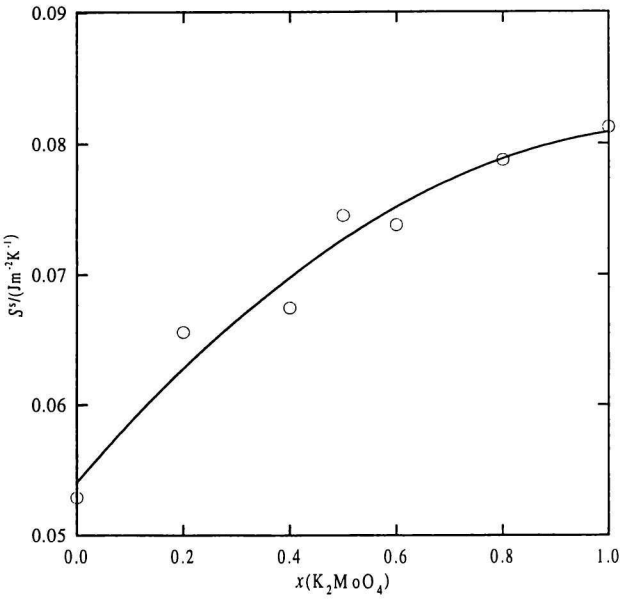

Fig. 6. Surface entropy in the binary system KF—K_2MoO_4.

surface tension of K_2MoO_4. However, the formation of polymerized molybdate polyanions may not be excluded.

The surface tension of the ternary system KF—K_2MoO_4—B_2O_3 at the temperature of 1100 K is shown in Fig. 4. The surface tension excess of this system at the same temperature is shown in Fig. 5. No significant ternary interaction was found. However, the above-mentioned reactions (*A*) and (*B*) take place obviously also in the ternary system.

In conclusion it should be emphasized that the surface tension data confirmed the conclusions drawn from the measurements of other physicochemical properties concerning the structure of the KF—K_2MoO_4—B_2O_3 melts.

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