Density of Melts of the System KF—K_2MoO_4—SiO_2

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The density of the melts of the system KF—K_2MoO_4—SiO_2 was measured using the Archimedean method. On the basis of the obtained density data the molar volume, partial molar volume, and excess molar volume of the melts were calculated in order to consider the possible chemical interactions of components.

In the system KF—K_2MoO_4 the density increases monotonically with increasing content of K_2MoO_4. The formation of the additive compound K_3FMoO_4 causes only small positive deviations from the ideal behaviour.

In the system KF—SiO_2 the density increases with increasing content of SiO_2. The partial molar volume of SiO_2 in the melt is a little higher than that of the pure SiO_2, which may refer to some weak chemical interaction of both components leading to a small volume expansion.

The density of the system K_2MoO_4—SiO_2 increases with increasing content of SiO_2. The partial molar volume of SiO_2 in the infinitely diluted solution, $\overline{V}_{SiO_2} = 3.65\ cm^3\ mol^{-1}$, may refer to a strong chemical interaction of both components accompanied by a substantial volume contraction.

Two different regions are present in the investigated part of the system KF—K_2MoO_4—SiO_2. In the region of low content of SiO_2, near the figurative point of K_3FMoO_4, there is a region of volume expansion, while at higher SiO_2 concentration a region of volume contraction is present. The volume expansion is caused by the formation of the additive compound K_3FMoO_4, while the volume contraction refers probably to the formation of the heteropolyanions $[SiMo_{12}O_{40}]^{4-}$.

The melts of the system KF—K_2MoO_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 as well as the network-forming one. The possible chemical interactions between them are not well understood.

Electrolytic molybdenum coating using the electrolytes of the system KF—K_2MoO_4—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. The quality of the deposit depends on the silica content in the melt. The authors explain the positive role of SiO_2 in the molybdenum electrodeposition by the change in the structure of the electrolyte and the formation in the melt of heteropolyanions $[SiMo_{12}O_{40}]^{4-}$ according to the reaction

$$12K_2MoO_4 + 7SiO_2 + 36KF = \\ = K_4\,[SiMo_{12}O_{40}] + 6K_2SiF_6 + 22K_2O \qquad (A)$$

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_2SiF_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 KF—K_2MoO_4—SiO_2 is a subsystem of the quinary reciprocal system K^+, Si^{4+}, $Mo^{6+}//F^-$, O^{2-}, in which a number of compounds may be formed. The phase diagram of the binary systems KF—K_2MoO_4, KF—SiO_2, and K_2MoO_4—SiO_2, as well as that of the ternary system KF—K_2MoO_4—SiO_2 in the range up to 50 mole % SiO_2, was measured in [3, 4]. In the system KF—K_2MoO_4 the intermediate compound K_3FMoO_4, melting congruently at 751 ℃, is formed. The compound divides the system into two simple eutectic ones the coordinates of which are: 29.4 mole % K_2MoO_4, 717.7 ℃ and 56.9 mole % K_2MoO_4, 747.4 ℃. In the binary system KF—SiO_2 the liquidus curve of KF shows an inflex point, characteristic of reciprocal systems with chemical reaction taking place between components. Similar course of the liquidus

Table 1. Coefficients a, b and the Standard Deviations of the Fits in the Temperature Dependence of Density in the System KF—K_2MoO_4—SiO_2

x_{KF}	$x_{K_2MoO_4}$	x_{SiO_2}	a / g cm^{-3}	$b \cdot 10^4$ / g cm^{-3} °C^{-1}	sd $\cdot 10^4$ / g cm^{-3}	t / °C
1.00	0.00	0.00	2.5579	7.5523	2.53	870—970
0.90	0.00	0.10	2.5665	7.1977	7.80	860—970
0.80	0.00	0.20	2.6130	7.3544	7.18	850—970
0.70	0.00	0.30	2.5015	6.8004	7.67	840—970
0.00	1.00	0.00	2.9189	6.1871	9.63	940—990
0.00	0.90	0.10	3.1834	8.5258	8.69	940—990
0.00	0.80	0.20	3.3196	9.6037	3.40	940—990
0.00	0.80	0.20	3.0926	7.6621	3.41	940—1000
0.72	0.18	0.10	2.7760	7.5530	5.74	860—960
0.54	0.36	0.10	2.6623	7.5348	5.46	850—970
0.36	0.54	0.10	2.9539	7.4946	3.70	870—950
0.18	0.72	0.10	2.9797	7.5348	4.72	900—1020
0.18	0.72	0.10	3.0168	7.4010	5.20	920—1040
0.64	0.16	0.20	2.7919	7.2104	7.50	850—970
0.64	0.16	0.20	2.8218	7.3336	6.50	850—970
0.48	0.32	0.20	2.9040	7.6849	9.25	860—990
0.48	0.32	0.20	2.8579	7.0653	8.72	860—990
0.32	0.48	0.20	2.8553	6.4150	6.75	900—1020
0.32	0.48	0.20	2.8746	6.5020	6.80	900—1020
0.16	0.64	0.20	3.0239	7.4179	8.39	900—1040
0.56	0.14	0.30	3.0387	7.9259	8.59	980—1070
0.42	0.28	0.30	3.1598	8.5503	9.18	1030—1100

curve of K_2MoO_4 was found in the binary system K_2MoO_4—SiO_2, indicating the presence of the chemical reaction between components as well. The strong positive deviation from ideal behaviour of the ternary system KF—K_2MoO_4—SiO_2 was ascribed to the possible formation of heteropolyanions $[SiMo_{12}O_{40}]^{4-}$ in the melt.

Quite recently, the surface tension of the KF—K_2MoO_4—SiO_2 melts was measured using the maximum bubble pressure method [5].

In the present work the density of melts of the ternary system KF—K_2MoO_4—SiO_2 was measured using the Archimedean method. On the basis of the obtained results the molar volume, partial molar volume of SiO_2, and the excess molar volume were calculated in order to obtain some information on the real ionic composition of the investigated melts.

EXPERIMENTAL

For the preparation of samples the following chemicals were used: KF (Lachema), K_2MoO_4 and SiO_2 (both Fluka), all anal. grade. KF was dried in vacuum 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 SiO_2 was remelted and crushed in an agate mortar. All handling and storage of the chemicals was done in the glove box.

The measurement was carried out in the temperature interval of approximately 100 K starting at 20—30 K above the temperature of primary crystallization. In the ternary system KF—K_2MoO_4—SiO_2 cross-sections with the constant mole ratio $x(KF)/x(K_2MoO_4)$ = 4, 1.5, 0.67, and 0.25 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.

The density of the investigated melts was measured using the Archimedean method. A platinum sphere suspended on a platinum wire has been used as the measuring body. The dependence of the sphere volume on temperature was determined by calibration using molten NaCl and KCl. For the measuring device control and the evaluation of experimental data the on-line PC XT computer was used. The experimental error in the density measurement did not exceed ± 0.4 %. The detailed description of the used measuring device may be found in [6]. The density was measured at cooling. The measuring device registered automatically the density values every 30 s. The measurement of every melt composition was 1—2 times repeated. The temperature dependences of the density are presented in the form of the linear equations

$$\rho = a - bt \qquad (1)$$

where ρ is the density in g cm^{3-} and t is the temperature in °C. The values of the constants a and b together with the standard deviations of approximations, obtained by the linear regression analysis of the experimentally obtained data, are given in Table 1.

RESULTS AND DISCUSSION

The density of the system KF—K_2MoO_4 was measured in [7]. The density in this system increases monotonically with increasing content of K_2MoO_4. From the values of the excess molar volume it follows that the system shows only small positive deviations from the ideal behaviour. This can be ascribed to the formation of the congruently melting compound K_3FMoO_4. The excess molar volume attains at $x(\mathrm{KF}) = 0.5$ the value $V^{\mathrm{ex}} = 1.94\ \mathrm{cm^3\ mol^{-1}}$ only, which indicates the pronounced thermal dissociation of the additive compound.

The obtained density data were used in the calculation of the degree of thermal dissociation of the additive compound K_3FMoO_4 in [8]. It was found that the degree of dissociation of K_3FMoO_4 attains the value $\alpha_\mathrm{o}(827\,^\circ\mathrm{C}) = 0.86$, which agrees very well with the value determined by the analysis of the phase diagram, $\alpha_\mathrm{o} = 0.81$ [8]. This value confirmed the assumption on the pronounced thermal dissociation of K_3FMoO_4 at melting.

The existence and structure of the complex anion $[FMoO_4]^{3-}$, however, may be a subject of discussion. Even when it cannot be identified by spectroscopic methods, obviously due to the weak Mo—F or O—F bonds and probably also a short lifetime, this complex anion can be considered as an associate. Its acceptance is well founded at least thermodynamically and serves as a useful example to understand the nature and behaviour of the investigated melts.

The concentration dependence of the molar volume of the KF—SiO_2 system at 1100 K can be described by the equation

$$\frac{V}{\mathrm{cm^3\ mol^{-1}}} = 30.084 - 3.6407x_{\mathrm{SiO_2}} - 3.5907x^2_{\mathrm{SiO_2}} \quad (2)$$

As it can be seen from the equation, the molar volume of the system KF—SiO_2 decreases with increasing content of SiO_2. Differentiating eqn (*2*) according to $x_{\mathrm{SiO_2}}$ and inserting into the equation

$$\overline{V}_{\mathrm{SiO_2}} = V + x_{\mathrm{KF}}\left(\frac{\partial V}{\partial x_{\mathrm{SiO_2}}}\right)_{p,T} \quad (3)$$

we get for the partial molar volume of SiO_2 the equation

$$\frac{\overline{V}_{\mathrm{SiO_2}}}{\mathrm{cm^3\ mol^{-1}}} = 26.4433 - 7.1814x_{\mathrm{SiO_2}} + 3.5907x^2_{\mathrm{SiO_2}} \quad (4)$$

For $x_{\mathrm{SiO_2}} \rightarrow 0$ we obtain for the partial molar volume of SiO_2 in the infinitely diluted solution the value $\overline{V}_{\mathrm{SiO_2}} = 26.44\ \mathrm{cm^3\ mol^{-1}}$. This value is a little higher than that of the pure SiO_2, $V^{\mathrm{o}}_{\mathrm{SiO_2}} = 22.85\ \mathrm{cm^3\ mol^{-1}}$, which may refer to some weak chemical interaction of both components leading to a small volume expansion. However, the nature of the chemical interaction could not be determined on the basis of the density measurement only.

The concentration dependence of the molar volume of the K_2MoO_4—SiO_2 system at 1100 K can be described by the equation

$$\frac{V}{\mathrm{cm^3\ mol^{-1}}} = 98.744 - 95.095x_{\mathrm{SiO_2}} + 19.209x^2_{\mathrm{SiO_2}} \quad (5)$$

From this equation it follows that the molar volume of the system K_2MoO_4—SiO_2 decreases with increasing content of SiO_2 as well. Differentiating eqn (*5*) according to $x_{\mathrm{SiO_2}}$ and inserting into the equation

$$\overline{V}_{\mathrm{SiO_2}} = V + x_{\mathrm{K_2MoO_4}}\left(\frac{\partial V}{\partial x_{\mathrm{SiO_2}}}\right)_{p,T} \quad (6)$$

we get for the partial molar volume of SiO_2 the equation

$$\frac{\overline{V}_{\mathrm{SiO_2}}}{\mathrm{cm^3\ mol^{-1}}} = 3.649 + 38.418x_{\mathrm{SiO_2}} - 19.209x^2_{\mathrm{SiO_2}} \quad (7)$$

For $x_{\mathrm{SiO_2}} \rightarrow 0$ we obtain for the partial molar volume of SiO_2 in the infinitely diluted solution the value $\overline{V}_{\mathrm{SiO_2}} = 3.65\ \mathrm{cm^3\ mol^{-1}}$. This value is much lower than that of the pure SiO_2, $V^{\mathrm{o}}_{\mathrm{SiO_2}} = 22.85\ \mathrm{cm^3\ mol^{-1}}$, which may refer to a strong chemical interaction of both components accompanied by a substantial volume contraction. Such behaviour can be explained by the formation in the melt of heteropolyanions $[SiMo_{12}O_{40}]^{4-}$ according to the reaction (*A*), as it was proposed in [1, 2].

The density of the system KF—K_2MoO_4—SiO_2 is shown in Fig. 1. The density increases almost monotonically from KF through K_2MoO_4 to SiO_2.

The dependence of the molar volume of the ternary system KF(1)—K_2MoO_4(2)—SiO_2(3) on composition at constant temperature can be described by the equation

$$V = \sum_{i=1}^{3} x_i V_i^{\mathrm{o}} + \sum_{i \neq j}^{3} x_i x_j \sum_{n=0}^{k} A_{nij} x_j^n + \sum_i B_i x_1^p x_2^q x_3^r \quad (8)$$

where p, q, r are adjustable integers. The first term represents ideal behaviour, the second one describes the binary interactions, and the third one the interaction of all three components. The constants V_i^{o}, A_{nij}, and B_i in eqn (*8*) were calculated using the multiple linear regression analysis omitting the statistically nonimportant terms on the 0.99 confidence level. The following equation was obtained

$$V = x_1V_1^{\mathrm{o}} + x_2V_2^{\mathrm{o}} + x_3V_3^{\mathrm{o}} + x_1x_2A_{011} + \\ + B_1x_1x_2^2x_3 + B_2x_1x_2x_3^2 \quad (9)$$

The values of constants V_i^{o}, A_{011}, and B_i in eqn (*9*) as well as the standard deviations of approximation

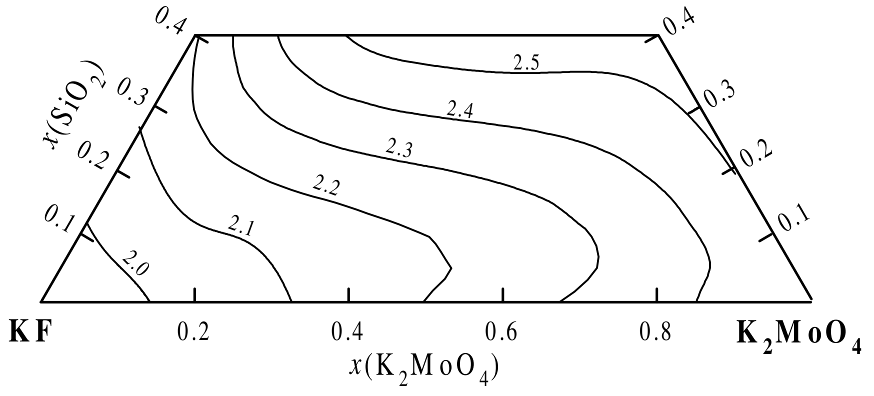

Fig. 1. Density/(g cm^{-3}) of melts of the system KF—K_2MoO_4—SiO_2 at 1100 K.

Table 2. Coefficients V_i^o, A_{nij}, and B_i of eqn (*3*) and the Standard Deviations of the Fit for the Composition Dependence of the Molar Volume of the System KF—K_2MoO_4—SiO_2

Constants	1100 K	1150 K	1200 K
$\frac{V_1^o}{\text{cm}^3\ \text{mol}^{-1}}$	30.52 ± 0.29	31.10 ± 0.29	31.71 ± 0.29
$\frac{V_2^o}{\text{cm}^3\ \text{mol}^{-1}}$	96.22 ± 0.76	97.90 ± 0.76	99.63 ± 0.76
$\frac{V_3^o}{\text{cm}^3\ \text{mol}^{-1}}$	22.91 ± 0.37	23.24 ± 0.37	23.58 ± 0.37
$\frac{A_{011}}{\text{cm}^3\ \text{mol}^{-1}}$	10.16 ± 2.90	10.94 ± 2.90	11.78 ± 2.93
$\frac{B_1}{\text{cm}^3\ \text{mol}^{-1}}$	256.5 ± 61.3	246.0 ± 61.3	234.6 ± 61.8
$\frac{B_2}{\text{cm}^3\ \text{mol}^{-1}}$	−479.0 ± 75.4	−487.6 ± 75.4	−496.5 ± 76.0
$\frac{\text{sd}}{\text{cm}^3\ \text{mol}^{-1}}$	0.73	0.73	0.74

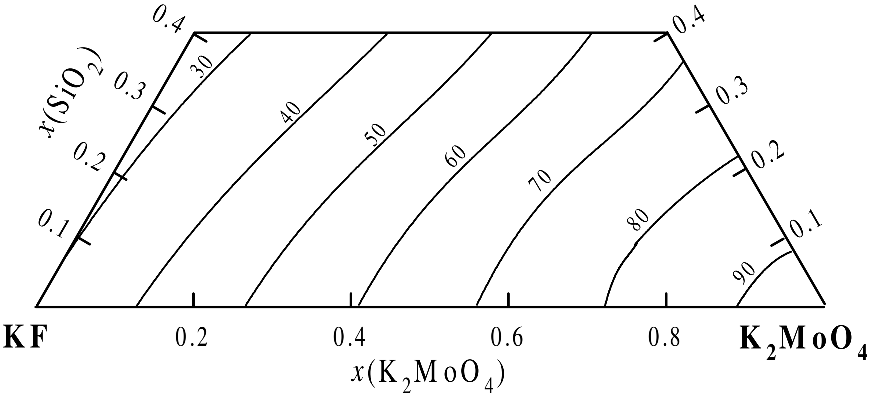

Fig. 2. Molar volume/(cm^3 mol^{-1}) of the system KF—K_2MoO_4—SiO_2 at 1100 K.

for the temperatures 1100 K, 1150 K, and 1200 K are given in Table 2. The molar volume of the system KF—K_2MoO_4—SiO_2 at the temperature of 1100 K is shown in Fig. 2 and the excess molar volume at the same temperature in Fig. 3.

As it can be seen from Fig. 3, two different regions are present in the investigated part of the system. In the region of low content of SiO_2, near the figurative point of K_3FMoO_4, there is a region of volume expansion, while at higher SiO_2 concentration a region of

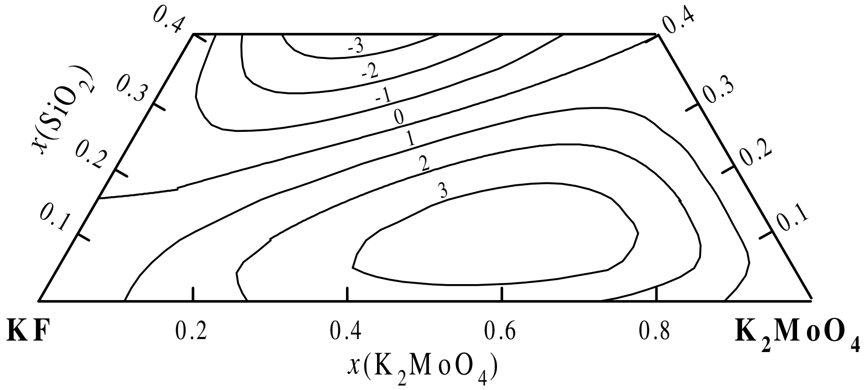

Fig. 3. Excess molar volume/(cm^3 mol^{-1}) of the system KF—K_2MoO_4—SiO_2 at 1100 K.

volume contraction is present. The volume expansion refers to the formation of more voluminous K_3FMoO_4 associates. On the other hand, the large volume contraction in the region of high SiO_2 concentration is most probably due to the loosing of free volume caused by the formation of a very big species. As it was suggested in [1, 2], this species may be the heteropolyanions $[SiMo_{12}O_{40}]^{4-}$ originating in the melt according to eqn (*A*). This assumption, however, must be confirmed by further investigation.

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