

Surface Tension of the System LiF—KF—K₂NbF₇

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The surface tension of the molten system LiF—KF—K₂NbF₇ has been determined using the maximum bubble pressure method. The error in the surface tension measurement was estimated to be $\pm 1.5\%$. 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 the possible chemical interaction of components was elucidated. The results are discussed in terms of the anionic composition.

From the obtained surface tension data the surface adsorption of K₂NbF₇ in the systems LiF—K₂NbF₇ and KF—K₂NbF₇ was calculated. The results indicated the presence of the surface-active [NbF₇]²⁻ and [NbF₈]³⁻ anions in the melt.

The melts of the system LiF—KF—K₂NbF₇ seem to be promising electrolytes for the electrodeposition of niobium from fused salts [1]. The interaction of components may lead to the formation of complex anions which serve as electroactive species, thus influencing the mechanism of the electrochemical process on the electrode surface.

The phase diagram of the system KF—K₂NbF₇ was studied in [2–4]. The congruently melting compound, K₃NbF₈, with the melting point according to different authors being in the range of 760–770 °C, gives rise to two eutectics. The coordinates of the respective eutectic points are according to different authors in the range 23–26.5 mole % K₂NbF₇, $t_e = 719$ – 732 °C, and 80–81 mole % K₂NbF₇, $t_e = 703$ – 708 °C. The melting point for K₂NbF₇ was determined to lie in the range 730–735 °C.

The phase diagrams of the systems LiF—K₂NbF₇ and LiF—KF—K₂NbF₇ were determined in [5]. The system LiF—K₂NbF₇ is a simple eutectic one with the coordinates of the eutectic point at 72 mole % K₂NbF₇ and 670 °C. In the system KF—K₂NbF₇ the intermediate compound K₃NbF₈, melting congruently at 770 °C, is formed. This compound divides the binary system KF—K₂NbF₇ into two simple eutectic ones the coordinates of which are: 25.3 mole % K₂NbF₇, $t_e = 725$ °C, and 81 mole % K₂NbF₇, $t_e = 707$ °C. In the ternary system LiF—KF—K₂NbF₇ the coordinates of the two ternary eutectic points are E₁: 22.3 mole % LiF, 9.4 mole % KF, 68.3 mole % K₂NbF₇; $t_e = 649$ °C, E₂: 45.5 mole % LiF, 51.7 mole % KF, 2.8 mole % K₂NbF₇; $t_e = 486$ °C.

In the present work the surface tension of the LiF—KF—K₂NbF₇ 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. The results are discussed in terms of the anionic composition.

EXPERIMENTAL

For the preparation of samples the following chemicals were used: LiF (Lachema), KF (Merck), and K₂NbF₇ (Aldrich), all of reagent quality. LiF was dried at 600 °C for 2 h, KF and K₂NbF₇ were dried in vacuum at 130 °C one day. All handling of salts was done in the glove box under a dry inert atmosphere.

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. The digital 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 [6]

$$\sigma = \frac{r}{2}(P_{\max} - gh_d) \quad (1)$$

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

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

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). T_m of the measured sample was taken from the previous phase diagram measurements [5]. The surface tension measurements were carried out at four different depths of immersion (usually 2.00, 3.00, 4.00, and 5.00 mm) yielding six surface tension values for each temperature.

In the ternary system LiF–KF–K₂NbF₇ cross-sections with the constant mole ratio $x(\text{LiF})/x(\text{KF}) = 0.333, 1, \text{ and } 3$, were chosen for the measurement. In the boundary binary systems and in the above-mentioned cross-sections the figurative points with the content of 25 mole %, 50 mole %, and 75 mole % K₂NbF₇ 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 (0.3–1.6) 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

$$\sigma = a - bT \quad (3)$$

where σ is the surface tension in mN m⁻¹ and T is the temperature in K. 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 LiF–KF–K₂NbF₇ melts are given in Table 1.

RESULTS AND DISCUSSION

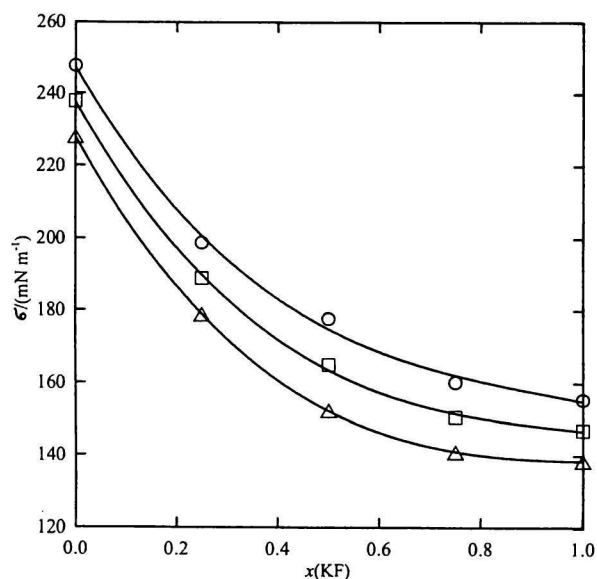
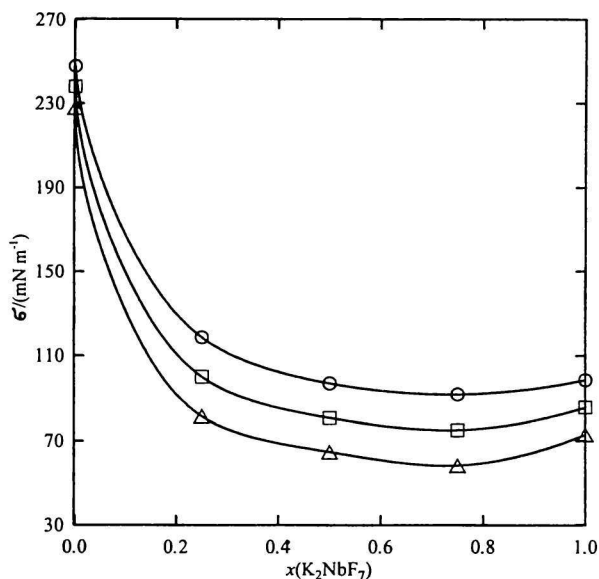
The surface tension reflects the nature of chemical bonds between species of the system being investigated. Due to the different coulombic interaction between species in the LiF–KF–K₂NbF₇ melts, the species being more covalent are concentrated on the surface and become surface-active. Therefore the anionic composition, especially the content of K₂NbF₇, forming the strongest covalent species, will influence substantially the composition dependence of the surface tension of these melts.

The surface tension of the boundary binary systems LiF–KF, LiF–K₂NbF₇, and KF–K₂NbF₇ at the temperatures 1000 K, 1100 K, and 1200 K is shown in Figs. 1–3, respectively. In the system LiF–KF the surface tension decreases with increasing content of KF obviously due to the lower polarizability of K⁺ cations. The decrease of the surface tension with increasing content of K₂NbF₇ in the systems LiF–K₂NbF₇ and KF–K₂NbF₇ is caused most probably by the more covalent character of the [NbF₇]³⁻ complex anions compared with that of the F⁻ ones. The former anions are thus surface-active and concentrate on the melt surface.

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

Table 1. Coefficients *a* and *b* of the Temperature Dependence of the Surface Tension, the Standard Deviations (SD) of Approximation, and the Temperature Range of Measurement of Individual Melts of the System LiF—KF—K₂NbF₇

<i>x</i> _{LiF}	<i>x</i> _{KF}	<i>x</i> _{K₂NbF₇}	<i>a</i>	<i>b</i>	SD	<i>T</i>
			mN m ⁻¹	mN m ⁻¹ K ⁻¹	mN m ⁻¹	K
1.000	0.000	0.000	346.50	0.09880	0.71	1141—1533
0.750	0.250	0.000	298.27	0.09957	1.60	973—1033
0.500	0.500	0.000	304.21	0.12665	0.62	1096—1149
0.250	0.750	0.000	256.42	0.09635	0.83	1027—1082
0.000	1.000	0.000	240.03	0.08478	0.35	1185—1583
0.000	0.750	0.250	217.44	0.09090	0.42	1030—1095
0.000	0.500	0.500	236.10	0.12175	1.06	1059—1110
0.000	0.250	0.750	232.18	0.12990	1.05	1033—1096
0.000	0.000	1.000	226.54	0.12774	0.44	1043—1063
0.250	0.000	0.750	261.07	0.16898	0.65	973—1033
0.500	0.000	0.500	259.02	0.16190	0.71	1061—1126
0.750	0.000	0.250	303.25	0.18463	0.92	1122—1186
0.563	0.187	0.250	284.48	0.15965	0.37	1018—1087
0.375	0.375	0.250	263.75	0.13640	0.15	918—968
0.187	0.563	0.250	247.39	0.11519	0.36	991—1054
0.375	0.125	0.500	249.05	0.13778	0.33	991—1060
0.250	0.250	0.500	212.34	0.13585	0.43	980—1037
0.125	0.375	0.500	195.79	0.10995	0.40	1009—1076
0.125	0.125	0.750	205.31	0.14535	0.48	970—1030

**Fig. 1.** Surface tension of the system LiF—KF. ○ 1000 K, □ 1100 K, Δ 1200 K, solid lines – calculated according to eqn (5).**Fig. 2.** Surface tension of the system LiF—K₂NbF₇. ○ 1000 K, □ 1100 K, Δ 1200 K, solid lines – calculated according to eqn (5).

composition was given by *Guggenheim* [9], who stated that the surface tension of an ideal solution should follow the simple additivity law 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

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

In eqn (4) the values σ_i are the surface tensions of pure

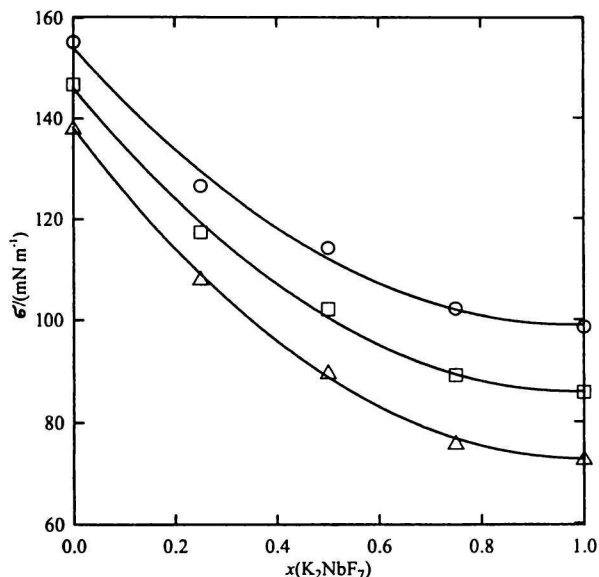


Fig. 3. Surface tension of the system KF—K₂NbF₇. ○ 1000 K, □ 1100 K, Δ 1200 K, solid lines – calculated according to eqn (5).

components and the values x_i are their mole fractions in the mixture. Coefficients a , b , c , n , and m 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 LiF(1)—KF(2)—K₂NbF₇(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

$$\begin{aligned} \sigma = & \sigma_1 x_1 + \sigma_2 x_2 + \sigma_3 x_3 + x_1 x_2 A_{012} + \\ & + x_1 x_3 (A_{013} + A_{113} x_3 + A_{213} x_3^2) + \\ & + x_2 x_3 A_{023} + x_1 x_2 x_3 B_1 \end{aligned} \quad (5)$$

Table 2. Coefficients σ_i , A_{nij} , B_m of the Composition Dependence of the Surface Tension of the System LiF(1)—KF(2)—K₂NbF₇(3) and the Standard Deviations of Approximation, SD, at Individual Temperatures

Coefficient	Temperature		
	1000 K	1100 K	1200 K
σ_1	244.05 ± 3.97	234.73 ± 4.10	224.88 ± 4.69
σ_2	154.62 ± 2.44	146.78 ± 2.48	139.36 ± 2.79
σ_3	98.86 ± 1.69	85.74 ± 1.60	72.81 ± 1.65
A_{012}	-94.89 ± 13.92	-106.51 ± 14.16	-116.59 ± 15.90
A_{013}	-777.06 ± 41.19	-874.83 ± 39.99	-966.73 ± 42.76
A_{113}	1449.16 ± 142.24	1720.84 ± 133.49	1981.55 ± 136.14
A_{213}	-965.44 ± 134.79	-1198.02 ± 124.74	-1428.28 ± 124.56
A_{023}	-58.72 ± 9.03	-61.07 ± 8.86	-69.66 ± 9.50
B_1	501.85 ± 60.06	564.49 ± 58.70	620.43 ± 62.83
SD	2.20	2.09	2.14

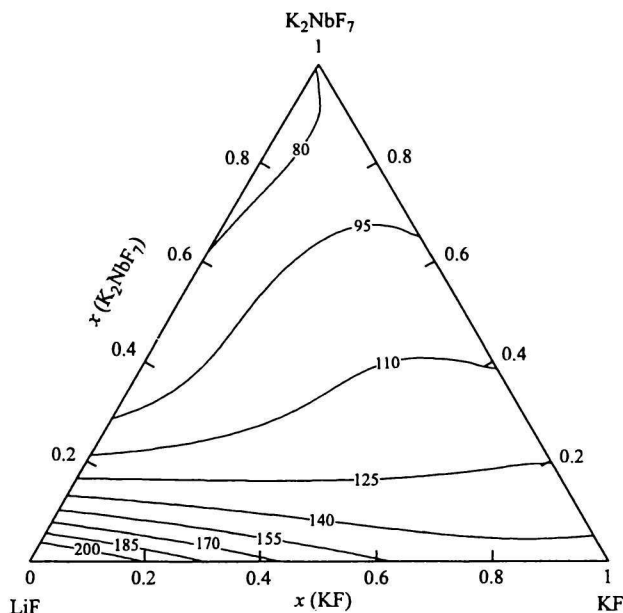


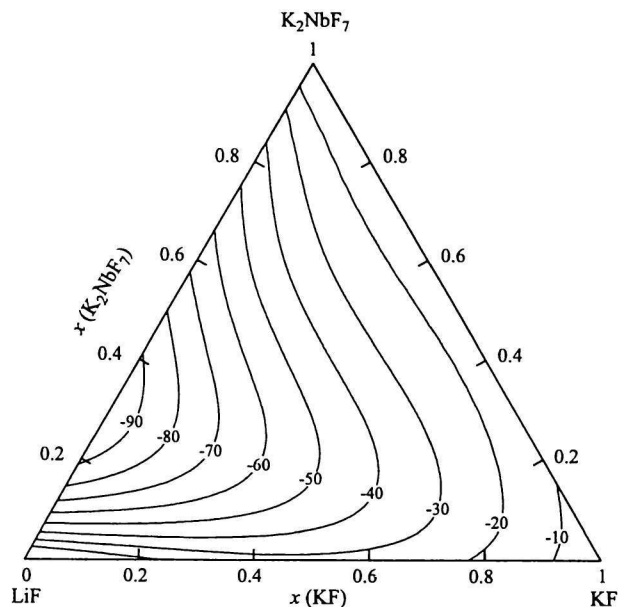
Fig. 4. Surface tension of the system LiF—KF—K₂NbF₇ at the temperature of 1100 K. Values are $\sigma/(\text{mN m}^{-1})$.

The values of the surface tension of pure components, σ_i , coefficients A_{nij} and B_1 , and the standard deviations of approximation for the chosen temperatures of 1000 K, 1100 K, and 1200 K are given in Table 2. The surface tension of the ternary system LiF—KF—K₂NbF₇ 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.

The binary interaction found in the system LiF—KF refers to the simple regular behaviour of this system, while the binary interaction in the system KF—K₂NbF₇ is obviously due to the formation of the complex anions $[\text{NbF}_8]^{3-}$. The binary interaction found in the system LiF—K₂NbF₇ and the ternary one found in the system LiF—KF—K₂NbF₇ have most probably the same reason.

Table 3. Parameters C_0 , C_1 , and B of the Composition Dependence of Surface Tension according to Eqn (8)

System	C_0	C_1	B
	mol m ⁻²	mol m ⁻²	J mol ⁻¹
LiF—K ₂ NbF ₇	3.495×10^{-8}	-1.717×10^{-6}	-1780
KF—K ₂ NbF ₇	1.782×10^{-5}	-1.736×10^{-5}	4000

Fig. 5. Surface tension excess of the system LiF—KF—K₂NbF₇ at the temperature of 1100 K. Values are $\sigma/(\text{mN m}^{-1})$.

The relations for the composition dependence of the surface tension and surface adsorption in ideal as well as regular binary mixtures were derived and discussed in [10]. As has been shown in that work, the calculation of the surface adsorption of K₂NbF₇ can be made either according to the equation

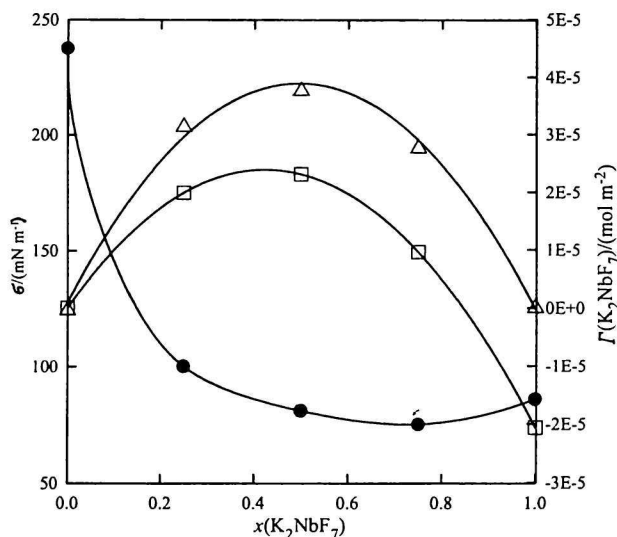
$$\Gamma_{\text{K}_2\text{NbF}_7} = \frac{\frac{x_{\text{K}_2\text{NbF}_7}}{RT} \frac{d\sigma}{dx_{\text{K}_2\text{NbF}_7}}}{1 + \frac{x_{\text{K}_2\text{NbF}_7}}{RT} \left(\frac{\partial^2(n\Delta_{\text{ex}}G)}{\partial n_2 \partial x_{\text{K}_2\text{NbF}_7}} \right)_{n_{\text{MF}}}} \quad (6)$$

using the excess Gibbs energy of mixing, $\Delta_{\text{ex}}G$, of the bulk liquid obtained *e.g.* from the thermodynamic analysis of the phase diagram, or from the equation

$$\Gamma_2 = x_2(C_0 + C_1x_2) \quad (7)$$

where the coefficients C_0 and C_1 can be obtained from the analysis of the composition dependence of surface tension expressed in the fourth-order polynomial form

$$\begin{aligned} \sigma = \sigma_1 + x_2(-RTC_0) + x_2^2 \frac{2BC_0 - RTC_1}{2} + \\ + x_2^3 \frac{2B(C_1 - C_0)}{3} + x_2^4 \frac{-2BC_1}{4} \end{aligned} \quad (8)$$

Fig. 6. Surface adsorption of K₂NbF₇ in the system LiF—K₂NbF₇. \square From phase diagram, Δ from surface tension. \bullet Surface tension of the system LiF—K₂NbF₇ at the temperature of 1100 K.

The calculation of the surface adsorption of K₂NbF₇ was made in the binary systems LiF—K₂NbF₇ and KF—K₂NbF₇. Both systems show simple eutectic phase diagrams not far from ideal behaviour. The Gibbs energy of mixing of both systems was taken from [5].

The polynomial coefficients of the composition dependence of the surface tension were obtained using the linear regression analysis of the experimentally determined data of surface tension on the 0.99 confidence level. Coefficients C_0 , C_1 , and B were then calculated from the polynomial coefficients and the obtained values are given in Table 3. The course of the composition dependence of the surface tension was then recalculated using eqn (8).

The surface adsorption of K₂NbF₇ was calculated according to eqn (7) using the calculated coefficients C_0 and C_1 and compared with that calculated according to eqn (6) inserting the excess Gibbs energy of mixing of the bulk liquid obtained from the phase diagram analysis. The results of the surface adsorption calculation for the systems LiF—K₂NbF₇ and KF—K₂NbF₇ are shown in Figs. 6 and 7, respectively. It can be seen from the figures that in both systems the

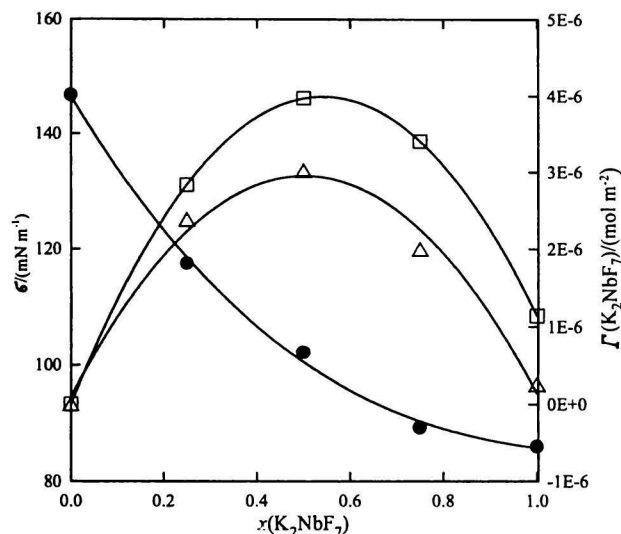


Fig. 7. Surface adsorption of K_2NbF_7 in the system $\text{KF}-\text{K}_2\text{NbF}_7$. □ From phase diagram, Δ from surface tension. ● Surface tension of the system $\text{KF}-\text{K}_2\text{NbF}_7$ at the temperature of 1100 K.

surface adsorption of K_2NbF_7 has a maximum approximately at 0.5 mole % K_2NbF_7 and is very similar in course regardless of the calculation procedure used. This indicates that the surface of the melt has very similar properties as the bulk liquid. The maximum in the surface adsorption course indicates the presence in the melt of even more surface-active species than the complex anions $[\text{NbF}_7]^{2-}$, which could be only the $[\text{NbF}_8]^{3-}$ ones. The last conclusion is also in accordance with the results of the phase diagram

measurements concerning the structure of the $\text{LiF}-\text{KF}-\text{K}_2\text{NbF}_7$ melts.

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