

# Surface Tension of Melts of the System KF—KCl—KBF<sub>4</sub>

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The surface tension of the molten system KF—KCl—KBF<sub>4</sub> has been determined using the maximum bubble pressure method. The error in the surface tension measurement was estimated to be  $\pm 1\%$ .

In the investigated system the surface tension decreases with increasing content of KBF<sub>4</sub>, which is apparently due to the surface adsorption of the BF<sub>4</sub><sup>-</sup> anions having stronger covalent character of bonds than the pure ionic KF and KCl melts. Moreover, the exchange of fluorine atoms in the BF<sub>4</sub><sup>-</sup> tetrahedra by the chlorine ones leads to the presence of the [BF<sub>4-n</sub>Cl<sub>n</sub>]<sup>-</sup> mixed anions which are adsorbed on the melt surface as well.

The calculated surface entropy in the binary systems has a maximum at the 1 : 1 mole ratio mixtures which increases from the system KF—KCl through KF—KBF<sub>4</sub> to KCl—KBF<sub>4</sub>. This indicates the simpler structure for the melts of pure components and of the system KF—KCl and the most complex one for those of the system KCl—KBF<sub>4</sub>.

The molten system KF—KCl—KBF<sub>4</sub> is an alternative electrolyte for electrochemical boriding of steels [1] and together with K<sub>2</sub>TiF<sub>6</sub> it serves as electrolyte for electrochemical synthesis of titanium diboride, especially to obtain protective layers on metallic substrates [2]. 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 affect the ionic composition, thus affecting the kind of the electroactive species. The suitable choice of the electrolyte composition may prevent the formation of volatile compounds, *e.g.* BCl<sub>3</sub>, which leads to undesirable exhalation and lowers the efficiency of the process.

The phase diagram of the system KF—KCl—KBF<sub>4</sub> was determined in [3]. The system is a simple eutectic one with the coordinates of the eutectic point of 19.4 mole % KF, 19.2 mole % KCl, 61.4 mole % KBF<sub>4</sub> and the temperature of the eutectic crystallization of 695 K. From among the physicochemical properties the density of this system was measured in [4], the electrical conductivity in [5], and the viscosity in [6]. On the basis of these measurements the substitution of the fluorine atoms in the BF<sub>4</sub><sup>-</sup> tetrahedron by the chlorine ones was suggested.

The surface tension reflects the nature of chemical bonds between species of the system being investi-

gated. Due to the different coulombic interaction between species in the KF—KCl—KBF<sub>4</sub> melts, the anions having more covalent character are concentrated on the surface and become surface-active. Therefore the anionic composition, especially the content of BF<sub>4</sub><sup>-</sup> anions, having the strongest covalent character, will influence substantially the concentration dependence of the surface tension of these melts.

In the present work the surface tension of the KF—KCl—KBF<sub>4</sub> 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 concentration dependence of the surface tension and of the surface tension excess of the investigated system was calculated and compared with the results of the 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), KCl and KBF<sub>4</sub> (both Fluka), all anal. grade. KF was dried in vacuum at 400 K in the presence of P<sub>2</sub>O<sub>5</sub> for two weeks, KCl and KBF<sub>4</sub> were dried at 680 K for 2 h. 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 po-

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sition 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.

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 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. 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. 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.

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  $\pm 1$  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 [7]

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

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 these 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 [3]. The surface tension measurements were carried out at four different depths of immersion (usually 2, 3, 4, and 5 mm) yielding six surface tension values for each temperature.

In the ternary system KF—KCl—KBF<sub>4</sub> cross-sections with the constant mole ratio  $x(\text{KF})/x(\text{KCl}) = 3, 1, \text{ and } 0.333$  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 % KBF<sub>4</sub> 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  $\pm 0.3\%$ . The determination of the immersion depth with an accuracy of  $\pm 0.01$  mm introduced an error of  $\pm 0.3\%$ . The accuracy of  $\pm 1$  Pa in the pressure measurement caused an additional error of  $\pm 0.4\%$ . The sum of all these errors gives an estimated total error of approx.  $\pm 1\%$ . The mean standard deviations of the experimental data based on the least-squares statistical analysis were in the range  $\pm (0.4\text{—}1.2)$  mN m<sup>-1</sup> 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 [8, 9] agreed within the estimated error.

The temperature dependence of the surface tension can be expressed by the linear equation

$$\sigma = a - b(T - 273) \quad (3)$$

where  $\sigma$  is the surface tension in mN m<sup>-1</sup> 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 KF—KCl—KBF<sub>4</sub> melts are given in Table 1.

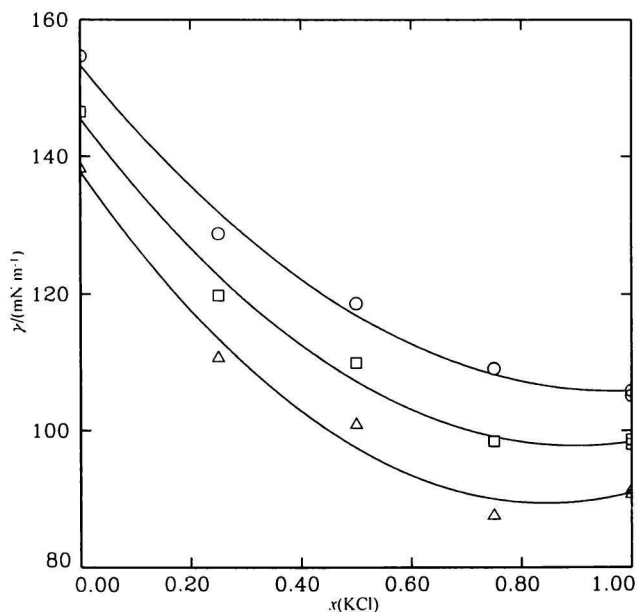
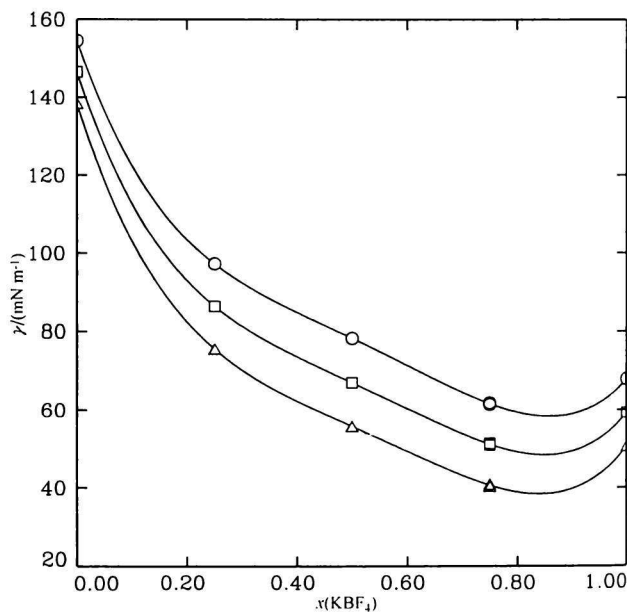
## RESULTS AND DISCUSSION

The surface tension of the boundary binary systems KF—KCl, KF—KBF<sub>4</sub>, and KCl—KBF<sub>4</sub> at the temperatures 1000 K, 1100 K, and 1200 K is shown in Figs. 1—3, respectively.

In the system KF—KCl the surface tension decreases with increasing content of KCl. This behaviour is due to the surface adsorption of Cl<sup>-</sup> anions which are less ionic in character than the F<sup>-</sup> ones. In the sys-

**Table 1.** Coefficients  $a$  and  $b$  of the Temperature Dependence of the Surface Tension, the Standard Deviations of Approximation, and the Temperature Range of Measurement of Individual Melts of the KF—KCl—KBF<sub>4</sub> System

$x_{\text{KF}}$	$x_{\text{KCl}}$	$x_{\text{KBF}_4}$	$a$	$b$	$sd$	$\langle T \rangle$
			mN m <sup>-1</sup>	mN m <sup>-1</sup> K	mN m <sup>-1</sup>	K
1.000	0.000	0.000	213.46	0.08088	0.72	1144—1223
0.750	0.250	0.000	193.99	0.08969	0.57	969—1168
0.500	0.500	0.000	182.47	0.08774	0.76	849—1043
0.250	0.750	0.000	186.27	0.10619	0.80	992—1060
0.000	1.000	0.000	156.47	0.07068	0.41	1077—1141
0.000	1.000	0.000	157.79	0.07147	0.56	1069—1138
0.750	0.000	0.250	176.32	0.10869	0.57	1083—1144
0.500	0.000	0.500	143.91	0.08373	0.54	957—1035
0.500	0.000	0.500	159.86	0.11223	0.54	973—1056
0.250	0.000	0.750	138.16	0.10492	0.84	759—843
0.250	0.000	0.750	137.75	0.10498	0.59	805—843
0.000	0.000	1.000	130.92	0.08661	1.16	860—975
0.000	0.750	0.250	168.22	0.10649	0.93	977—1067
0.000	0.500	0.500	178.23	0.14136	0.87	891—956
0.000	0.250	0.750	144.79	0.11209	0.58	762—839
0.187	0.563	0.250	156.01	0.08902	1.00	1014—1083
0.375	0.375	0.250	150.30	0.08181	0.85	881—957
0.563	0.187	0.250	149.09	0.08218	0.79	912—993
0.125	0.375	0.500	129.99	0.08201	0.44	869—962
0.250	0.250	0.500	134.99	0.08636	0.51	792—883
0.375	0.125	0.500	129.61	0.07689	0.51	852—940
0.063	0.187	0.750	119.99	0.08195	0.69	764—860
0.125	0.125	0.750	119.01	0.08010	0.65	789—863
0.187	0.063	0.750	120.02	0.08100	0.44	793—860

**Fig. 1.** Surface tension of the system KF—KCl. ○ 1000 K; □ 1100 K; △ 1200 K, solid lines – calculated according to eqn (5).**Fig. 2.** Surface tension of the system KF—KBF<sub>4</sub>. ○ 1000 K; □ 1100 K; △ 1200 K, solid lines – calculated according to eqn (5).

tems KF—KBF<sub>4</sub> and KCl—KBF<sub>4</sub> the surface tension decreases with increasing content of KBF<sub>4</sub> obviously due to the covalent character of the BF<sub>4</sub><sup>-</sup> complex anions, which are 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 surface tension course of the ideal solution. A general approach used

**Table 2.** Coefficients  $\sigma_i$ ,  $A_{nij}$ ,  $B_m$  of the Concentration Dependence of the Surface Tension of the System KF(1)—KCl(2)—KBF<sub>4</sub>(3) and the Standard Deviations of Approximation, sd, at Individual Temperatures

Coefficient	Temperature		
	1000 K	1100 K	1200 K
mN n <sup>-1</sup>			
$\sigma_1$	152.91 ± 2.23	144.37 ± 2.55	137.26 ± 3.33
$\sigma_2$	105.67 ± 1.15	98.41 ± 1.31	91.10 ± 1.72
$\sigma_3$	68.07 ± 1.07	59.57 ± 1.15	51.13 ± 1.36
$A_{012}$	-48.69 ± 7.82	-54.06 ± 8.63	-65.94 ± 11.12
$A_{013}$	-318.36 ± 28.23	-311.54 ± 28.24	-341.24 ± 35.30
$A_{113}$	668.99 ± 95.31	594.47 ± 96.67	638.23 ± 118.38
$A_{213}$	-586.33 ± 84.94	-515.87 ± 87.69	-541.95 ± 106.20
$A_{023}$	-106.95 ± 7.93	-118.88 ± 9.39	-114.11 ± 7.91
$A_{123}$	114.21 ± 15.73	98.98 ± 17.61	
$A_{223}$			89.39 ± 23.90
$B_0$		238.18 ± 39.51	390.45 ± 47.28
$B_1$	1401.58 ± 368.34		
sd	1.26	1.34	1.58

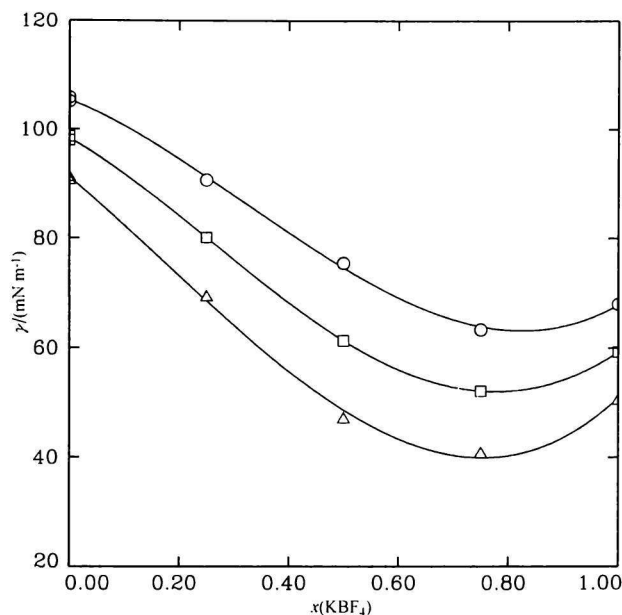
for the variation of surface tension with composition was given by *Guggenheim* [10], who stated that the surface tension of an ideal solution should follow the simple additivity formula to a good approximation. To describe the excess surface tension in the real system Redlich—Kister's type excess function can be used. For the surface tension of the real ternary system it can then be written

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

In eqn (4)  $\sigma_i$ 's are the surface tensions of pure components and  $x_i$ 's are their mole fractions in the mixture. Coefficients  $a$ ,  $b$ ,  $c$  are integers in the range 0—3. 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)—KCl(2)—KBF<sub>4</sub>(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

$$\begin{aligned} \sigma/(\text{mN/m}) = & \sigma_1 x_1 + \sigma_2 x_2 + \sigma_3 x_3 + x_1 x_2 A_{012} + \\ & + x_1 x_3 (A_{013} + A_{113} x_3 + A_{213} x_3^2) + \\ & + x_2 x_3 (A_{023} + A_{123} x_2 + A_{223} x_2^2) + \\ & + x_1 x_2 x_3 (B_0 + B_1 x_1 x_2) \end{aligned} \quad (5)$$

Surface tensions  $\sigma_i$  of pure components, coefficients  $A_{nij}$  and  $B_m$ , 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 KF—KCl—KBF<sub>4</sub> at the

**Fig. 3.** Surface tension of the system KCl—KBF<sub>4</sub>. ○ 1000 K; □ 1100 K; △ 1200 K, solid lines - calculated according to eqn (5).

temperature of 1100 K is shown in Fig. 4. The surface tension excess of this system is shown in Fig. 5.

As it was found out previously [3—6], the interaction of components may be of different origin. With regard to the fact that the investigated system has a common cation, the determined deviations from the ideal behaviour must be a consequence of the anionic interaction. First of all a different character of interaction has to be considered in the boundary binaries KF—KBF<sub>4</sub> and KCl—KBF<sub>4</sub>.

In the pure KBF<sub>4</sub> melt BF<sub>4</sub><sup>-</sup> tetrahedra tend to link, forming relatively weak B—F—B bonds. The

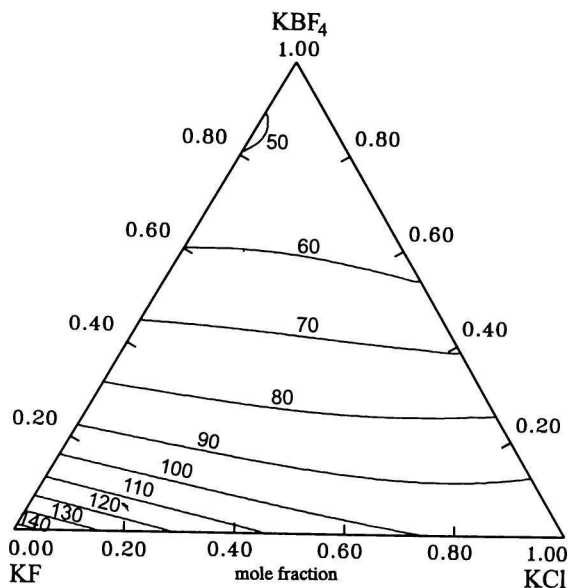


Fig. 4. Surface tension of the system KF–KCl–KBF<sub>4</sub> at the temperature of 1100 K. Surface tension values are in mN m<sup>-1</sup>.

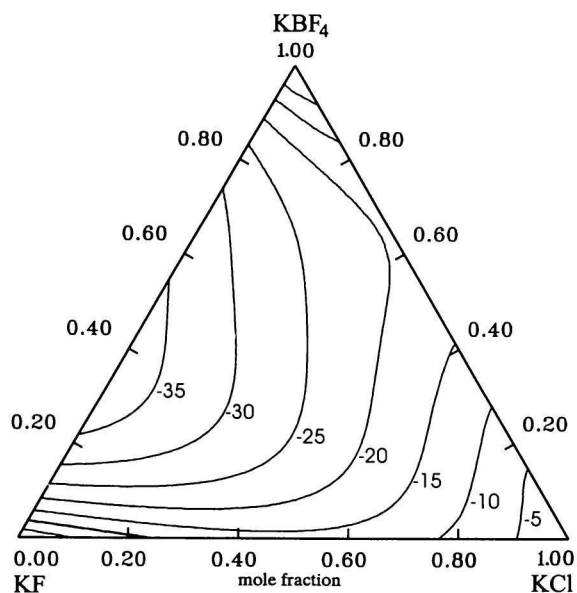
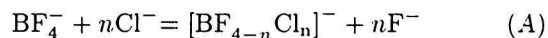


Fig. 5. Excess surface tension of the system KF–KCl–KBF<sub>4</sub> at the temperature of 1100 K. Values are in mN m<sup>-1</sup>

strength of this bond depends strongly on temperature. Introducing F<sup>-</sup> ions into the KBF<sub>4</sub> melt by addition of KF, the B–F–B bridges break off, which leads to the negative deviation of the surface tension in the KF–KBF<sub>4</sub> system and the adsorption of BF<sub>4</sub><sup>-</sup> anions on the surface.

In the system KCl–KBF<sub>4</sub> the exchange of fluorine atoms in the BF<sub>4</sub><sup>-</sup> tetrahedra for the chlorine ones according to the general scheme



and the probable presence of the [BF<sub>4-n</sub>Cl<sub>n</sub>]<sup>-</sup> mixed anions may be achieved. These anions are adsorbed on the melt surface as well. The lower stability of the B–Cl–B bridges and the lower concentration of the B–F–B ones lead to the negative deviations of the surface tension in the KCl–KBF<sub>4</sub> system. This explanation is supported also by the asymmetric course of the surface tension which is due to the shift of reaction (A) to the right side in the region of high concentration of KBF<sub>4</sub>.

For a system in chemical equilibrium at constant pressure the Gibbs equation for the surface tension is valid [11]

$$d\sigma = -S^s dT - \sum \Gamma_i d\mu_i \quad (8)$$

where  $\sigma$  is the surface tension,  $S^s$  is the surface entropy,  $\Gamma_i$  is the relative surface adsorption, and  $\mu_i$  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

$$S^s = - \left[ \frac{d\sigma}{dT} \right]_{\mu_j} \quad (9)$$

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

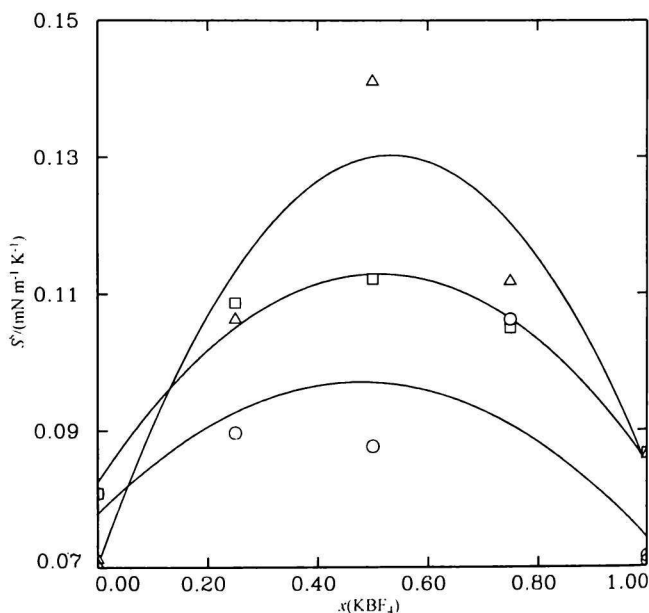


Fig. 6. Surface entropy of the investigated binary systems. ○ KF–KCl; □ KF–KBF<sub>4</sub>; △ KCl–KBF<sub>4</sub>.

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 (9) we can see 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 systems is shown. The surface entropy has a maximum at the 1 : 1 mixtures, which reflects the relative simple structure of the melts of pure components in comparison with that of the mixtures. Simultaneously this maximum increases from the system KF—KCl through KF—KBF<sub>4</sub> to KCl—KBF<sub>4</sub>, which obviously indicates the more ordered structure for the melts of the system KF—KCl and the most complex one for those of the system KCl—KBF<sub>4</sub>.

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—KCl—KBF<sub>4</sub> melts.

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