

Densities of Melts of the System LiF—KF—B₂O₃—TiO₂

M. CHRENKOVÁ, V. DANĚK, and A. SILNÝ

Institute of Inorganic Chemistry, Slovak Academy of Sciences, CS-842 36 Bratislava

Received 26 November 1991

Introducing B₂O₃ into molten LiF, lithium metaborate and volatile BF₃, which escapes from the melt, are formed. This leads to the volume contraction. In the system KF—B₂O₃ the addition of B₂O₃ into molten KF leads to the formation of more polymerized potassium tetraborate and KBF₄ which causes the volume expansion. The dependence of the molar volume on composition in the ternary system LiF—KF—B₂O₃ and the quaternary system LiF—KF—B₂O₃—TiO₂ was described.

The study of the volume properties of the melts of the quaternary system LiF—KF—B₂O₃—TiO₂ is a part of the complex physicochemical analysis of this system, which is interesting as an alternative electrolyte for the electrochemical synthesis of titanium diboride, especially for the preparation of finely dispersed powders [1].

The phase equilibria in the system LiF—KF—B₂O₃—TiO₂ were determined and the structure of the melts was elucidated in detail in the previous papers [2, 3]. From the cited works it follows that in the region of the primary crystallization of LiF in the ternary system LiF—KF—B₂O₃ a liquid miscibility gap is formed at compositions from 5 to 23 mole % B₂O₃ in the LiF—B₂O₃ boundary system and up to 12 mole % KF in the ternary one. From the thermodynamic analysis of the binary systems it follows that the dissolution of boron oxide in molten lithium fluoride leads to the formation of Li₂B₄O₇ while in molten potassium fluoride the compounds KBF₄ and K₂B₄O₇ are formed. These compounds are most probably present also in the melts of the ternary system. By addition of TiO₂ into molten LiF or into molten LiF—KF mixtures insoluble Li₂TiO₃ precipitates immediately from the melt. The increase of the liquidus temperature after addition of TiO₂ is most probably due to the primary crystallization of Li₂TiO₃.

From the density data only those of the pure components LiF, KF, and B₂O₃ as well as of the melts of the binary system LiF—KF can be found in the literature [4].

EXPERIMENTAL

Densities of the investigated melts were determined by the Archimedean method. The detailed description of the measuring device is given in [5]. A platinum cylinder with the diameter of 15 mm

and the height of 20 mm was used as the measuring body. The mass difference of the cylinder in the melt and in air was registered using the automatic balance. The dependence of the cylinder volume on the temperature was determined by calibration using the known density values of molten sodium and potassium chlorides. The error in the density measurement was ± 0.4 %. The density measurements in the binary systems LiF—B₂O₃ and KF—B₂O₃ were realized only up to 25 and 20 mole % B₂O₃, respectively. Owing to the increased viscosity of the melts the density measurement at higher contents of boron oxide using the Archimedean method shows considerably lowered precision. In the ternary system LiF—KF—B₂O₃ the mixtures with the constant mole fractions ratio $x(\text{LiF})/x(\text{KF}) = 0.33, 1, 3$ and with 10 and 20 mole % B₂O₃, respectively, were measured. In the system LiF—KF only the density of the mixture with 50 mole % KF was measured. The additional values were taken from the literature. With respect to the low solubility of titanium(IV) oxide in the melts of the system LiF—KF—B₂O₃ only the cross-section with the constant content of 5 mole % TiO₂ was measured. Since titanium(IV) oxide is not soluble in molten LiF and LiF—KF mixtures (Li₂TiO₃ precipitates from the melt) the density of these melts was not measured.

The experimentally determined temperature dependences of the density were described by the linear equations

$$\rho = a - b\theta \quad (1)$$

The values of the constants a and b and the standard deviations of approximation are summarized in Table 1. From the measured density values the molar volumes and the excess molar volumes of the investigated melts were calculated.

Table 1. Constants *a* and *b* in Eqn (1) and the Standard Deviation of Approximation for the Investigated Melts

<i>x</i> (LiF)	<i>x</i> (KF)	<i>x</i> (B ₂ O ₃)	<i>x</i> (TiO ₂)	<i>a</i>	<i>b</i> · 10 ⁴	<i>s</i> · 10 ⁴
				g cm ⁻³	g cm ⁻³ °C ⁻¹	g cm ⁻³
0.500	0.500	—	—	2.2624	4.4449	0.231
0.950	—	0.050	—	2.3117	5.7415	3.244
0.900	—	0.100	—	2.3222	5.9266	0.592
0.800	—	0.200	—	2.4308	6.6845	0.364
0.750	—	0.250	—	2.4440	6.8290	2.756
—	0.900	0.100	—	2.1247	3.9221	2.535
—	0.800	0.200	—	1.8462	1.1206	0.935
0.225	0.675	0.100	—	2.3440	5.2001	1.902
0.360	0.540	0.100	—	2.3235	4.2896	3.050
0.450	0.450	0.100	—	2.3780	4.6002	2.306
0.675	0.225	0.100	—	2.3099	5.2760	0.390
0.810	0.090	0.100	—	2.3024	5.4348	2.356
0.200	0.600	0.200	—	2.4876	5.0624	3.750
0.320	0.480	0.200	—	2.5454	5.0112	2.608
0.400	0.400	0.200	—	2.6240	5.6513	2.502
0.600	0.200	0.200	—	2.4700	5.7002	1.496
0.720	0.080	0.200	—	2.3962	5.9003	3.070
—	0.950	—	0.050	2.2911	4.0617	0.776
—	0.855	0.095	0.050	2.0978	2.4262	0.547
—	0.760	0.190	0.050	2.4309	1.8507	3.186
0.214	0.641	0.095	0.050	2.4309	4.2622	0.435
0.428	0.428	0.095	0.050	2.4416	4.9788	1.183
0.641	0.214	0.095	0.050	2.3376	4.6925	0.651
0.190	0.570	0.190	0.050	2.3825	4.1183	0.420
0.380	0.380	0.190	0.050	2.5508	6.3710	1.932
0.570	0.190	0.190	0.050	2.4026	5.2061	0.478

RESULTS AND DISCUSSION

The System MF—B₂O₃

From the data given in Table 1 it follows that the addition of B₂O₃ into the molten LiF causes the increase in the density, while the addition of B₂O₃ into molten KF leads to the density decrease. The molar volumes in both the systems are shown in Fig. 1. Again a different behaviour can be observed. The system LiF—B₂O₃ shows negative deviations from the ideal mixing ($V_m^{\circ}(\text{B}_2\text{O}_3, 850\text{ }^{\circ}\text{C}) = 44.78\text{ cm}^3\text{ mol}^{-1}$) and the deviations from ideality in the KF—B₂O₃ one are positive. The different behaviour of B₂O₃ in molten LiF and KF can be explained by means of the values of the partial molar volumes of B₂O₃ in both dilute solutions.

The dependence of the molar volume on the composition of melts in the systems MF—B₂O₃ can be described by the general equation

$$V_m = A + B x(\text{B}_2\text{O}_3) + C x^2(\text{B}_2\text{O}_3) \quad (2)$$

The values of the constants *A*, *B*, and *C* for the temperature of 850 °C are given in Table 2. In the system LiF—B₂O₃ a linear dependence for $x(\text{B}_2\text{O}_3) \leq 0.25$ was obtained, while in the system KF—B₂O₃ the second-degree dependence for $x(\text{B}_2\text{O}_3) \leq 0.20$ is the best fitted. The partial molar

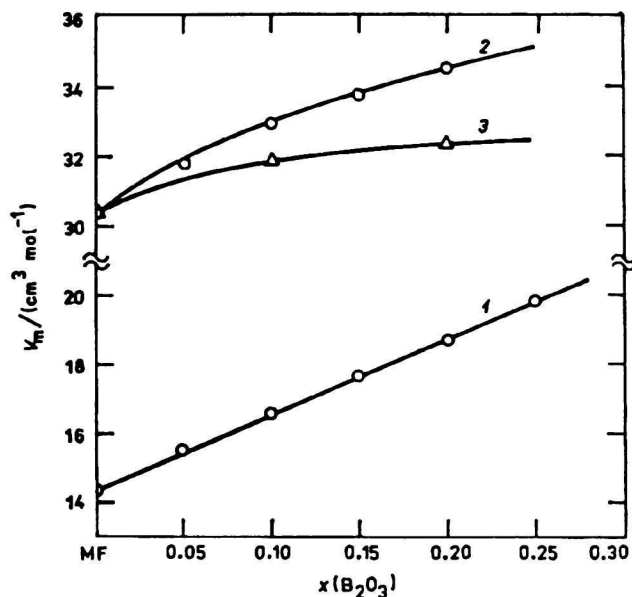


Fig. 1. Molar volume of melts in the binary and ternary systems at 850 °C. 1. LiF—B₂O₃; 2. KF—B₂O₃; 3. KF—B₂O₃—5 mole % TiO₂.

volume of B₂O₃ can be calculated according to the equation

$$V_m(\text{B}_2\text{O}_3) = V_m + x(\text{MF}) \left[\frac{\partial V_m}{\partial x(\text{B}_2\text{O}_3)} \right]_{\theta, p} \quad (3)$$

Differentiating eqn (2) and introducing it into eqn (3) we get for the partial molar volume of B₂O₃ in the system LiF—B₂O₃ at 850 °C the value $V_m(\text{B}_2\text{O}_3) = 35.84\text{ cm}^3\text{ mol}^{-1}$. For the partial molar volume of B₂O₃ in the system KF—B₂O₃ at 850 °C the equation

$$V_m(\text{B}_2\text{O}_3) = 9.94 + 51.31 x^2(\text{KF}) \quad (4)$$

was obtained, which gives the value $V_m(\text{B}_2\text{O}_3) = 61.25\text{ cm}^3\text{ mol}^{-1}$ in the infinitely diluted solution of B₂O₃ in molten KF. This value is substantially higher than the respective value in molten LiF.

From the physical point of view the partial molar volume of B₂O₃ in the dilute solution of MF represents the volume increase caused by the addition of the first molecules of B₂O₃ into a great surplus

Table 2. Constants *A*, *B*, and *C* in Eqn (2) and the Standard Deviation of Approximation for the Studied Systems at 850 °C

Constant	LiF—B ₂ O ₃	KF—B ₂ O ₃	KF—B ₂ O ₃ + 5 mole % TiO ₂
cm ³ mol ⁻¹			
<i>A</i>	14.365 ± 0.036	30.355 ± 0.034	30.422 ± 0.023
<i>B</i>	21.573 ± 0.241	30.899 ± 0.801	19.991 ± 0.573
<i>C</i>	—	-51.314 ± 3.841	-52.624 ± 2.890
<i>s</i> /(cm ³ mol ⁻¹)	0.045	0.025	0.017

of MF. The different values of the partial molar volume of B_2O_3 in both solvents thus confirm the findings obtained in the phase equilibria study [2, 3]. Lithium metaborate and volatile BF_3 , which escapes from the melt, are formed, when B_2O_3 is added into molten LiF. The volume increase is lower compared with the molar volume of pure B_2O_3 (see constant A_3 in Table 3). This leads to the volume contraction.

In the system KF— B_2O_3 the addition of B_2O_3 into the molten KF leads to the formation of more polymerized potassium tetraborate and KBF_4 , which causes the volume expansion. The volume increase is higher than the molar volume of pure B_2O_3 .

The Ternary System LiF—KF— B_2O_3

The molar volume of melts of the system LiF—KF— B_2O_3 at the temperature of 850 °C is shown in Fig. 2. From the figure it follows that the deviations from the ideal behaviour in the ternary system are more evident in comparison with the binary systems. In both investigated cross-sections

which represents 20.5 % of the molar volume at this composition. Such high deviations from ideal mixing indicate a strong interaction of all components. Therefore, the dependence of the molar volume on composition in the ternary system LiF—KF— B_2O_3 was described by the general equation

$$V_m = \sum_{i=1}^3 A_i x_i + \sum_{i \neq j}^3 x_i x_j (B_{ij} + C_{ij} x_j) + x_1 x_2 x_3 D \quad (5)$$

The first member represents the ideal mixing, the second one the binary interactions and the third one the mutual interaction of all three components. Using the multiple linear regression analysis and omitting the statistically nonimportant members at the 0.95 confidence level the following final equation was obtained

$$V_m = A_1 x(\text{LiF}) + A_2 x(\text{KF}) + A_3 x(B_2O_3) + x(\text{LiF}) x(\text{KF}) [B_{12} + C_{12} x(\text{KF})] + x(\text{LiF}) x(B_2O_3) [B_{13} + C_{23} x(B_2O_3)] + x(\text{KF}) x(B_2O_3) [B_{23} + C_{23} x(B_2O_3)] + x(\text{LiF}) x(\text{KF}) x(B_2O_3) D \quad (6)$$

The regression coefficients A_i , B_{ij} , C_{ij} , D and the standard deviations of approximation for the tem-

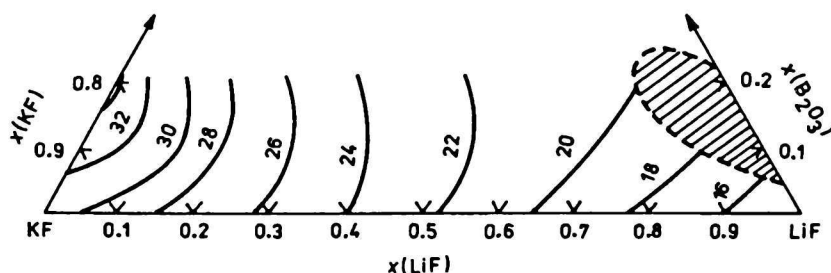


Fig. 2. Molar volume of melts of the ternary system LiF—KF— B_2O_3 at 850 °C. The dotted curve shows the immiscibility region.

Table 3. Constants A_i , B_{ij} , C_{ij} , and D in Eqn (6) and the Standard Deviations of Approximation for the LiF—KF— B_2O_3 System

Constant	$\theta/^\circ\text{C}$		
$\text{cm}^3 \text{mol}^{-1}$	800	850	900
A_1	14.164 ± 0.352	14.421 ± 0.311	14.566 ± 0.276
A_2	29.516 ± 0.431	30.061 ± 0.380	30.621 ± 0.338
A_3	44.433 ± 0.473	44.771 ± 0.417	45.621 ± 0.371
B_{12}	15.239 ± 4.322	15.186 ± 3.815	14.108 ± 3.397
B_{23}	31.715 ± 9.205	34.783 ± 8.126	36.571 ± 7.235
B_{13}	-10.119 ± 2.619	-10.876 ± 2.312	-9.054 ± 2.059
C_{12}	-25.087 ± 7.490	-25.909 ± 6.612	-25.878 ± 5.887
C_{23}	-120.076 ± 43.16	-144.378 ± 38.10	-162.687 ± 33.92
D	-147.370 ± 16.93	-140.525 ± 14.95	-140.311 ± 13.31
s^*	0.372	0.328	0.292

* /($\text{cm}^3 \text{mol}^{-1}$).

the maximum excess molar volume was observed at the content of 50 mole % KF. For instance, in the cross-section with the constant content of 20 mole % B_2O_3 the value $V_m(\text{ex}) = 4.62 \text{ cm}^3 \text{mol}^{-1}$,

peratures of 800, 850, and 900 °C are given in Table 3. The coefficients A_i are equal evidently to the values of the molar volumes of pure components. From the values of the standard deviation of approximation it follows that the obtained equation satisfactorily describes the course of the molar volume in the investigated part of the ternary system. The binary and the ternary interaction terms in the binary system MF— B_2O_3 correspond to the mutual chemical reaction of components under formation of gaseous BF_3 and the lithium borate in the case of LiF and of KBF_4 and the potassium borate in the case of KF.

The System LiF—KF— B_2O_3 — TiO_2

The molar volume of the cross-section of the ternary system KF— B_2O_3 — TiO_2 with constant content of 5 mole % TiO_2 at the temperature of 850

Table 4. Constants A_i , B_{ij} , and D_{ijk} in Eqn (8) and the Standard Deviations of Approximation for the Investigated Part of the System LiF—KF—B₂O₃—TiO₂

Constant	$\theta/^\circ\text{C}$		
	800	850	900
$\text{cm}^3 \text{ mol}^{-1}$			
A_1	14.209 ± 0.419	14.374 ± 0.423	14.572 ± 0.447
A_2	29.840 ± 0.442	30.314 ± 0.447	30.817 ± 0.472
A_3	44.436 ± 0.442	44.778 ± 0.447	45.157 ± 0.472
A_4	20.002 ± 0.442	20.001 ± 0.447	20.001 ± 0.472
B_{13}	14.498 ± 7.692	14.163 ± 7.783	13.890 ± 8.213
B_{24}	19.354 ± 11.38	18.220 ± 11.51	12.397 ± 12.15
D_{123}	-136.749 ± 25.76	-129.564 ± 26.06	-123.398 ± 27.50
s^*	0.312	0.316	0.334

* /($\text{cm}^3 \text{ mol}^{-1}$).

$^\circ\text{C}$ is shown in Fig. 1. The values of the constants A , B , and C of eqn (2) for the dependence of the molar volume on composition are given in Table 2. From the figure it follows that the addition of titanium(IV) oxide into the KF—B₂O₃ melt decreases the molar volume of the mixtures. However, the excess molar volume in this case is also negative.

In the calculation of the additive and the excess molar volumes in the investigated cross-sections of the quaternary system LiF—KF—B₂O₃—TiO₂ the molar volume of pure TiO₂ at the experimental temperature had to be estimated. The value $V_m(\text{TiO}_2) = 20 \text{ cm}^3 \text{ mol}^{-1}$, frequently used as the average value for silicate glasses [6], was chosen.

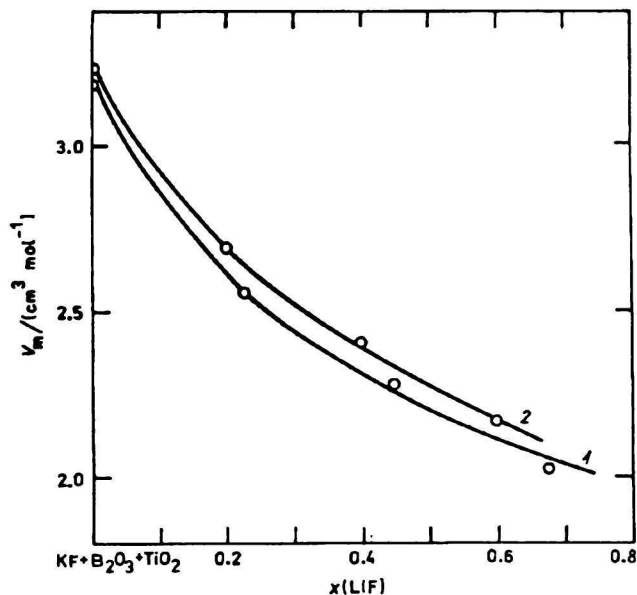
For the dependence of the molar volume on composition in the quaternary system LiF—KF—B₂O₃—TiO₂ the following general equation was used

$$V_m = \sum_{i=1}^4 A_i x_i + \sum_{i \neq j}^4 x_i x_j B_{ij} + \sum_{i \neq j \neq k}^4 x_i x_j x_k D_{ijk} \quad (7)$$

Again the first member represents the ideal mixing, the second one the binary interactions and the third one the mutual interactions of three components. The interaction of all four components was not considered. Using the multiple linear regression analysis and omitting the statistically non-important members at the 0.95 confidence level the following final equation was obtained

$$V_m = A_1 x(\text{LiF}) + A_2 x(\text{KF}) + A_3 x(\text{B}_2\text{O}_3) + A_4 x(\text{TiO}_2) + B_{13} x(\text{LiF}) x(\text{B}_2\text{O}_3) + B_{24} x(\text{KF}) x(\text{TiO}_2) + D_{123} x(\text{LiF}) x(\text{KF}) x(\text{B}_2\text{O}_3) \quad (8)$$

The regression coefficients A_i , B_{ij} , D_{ijk} and the standard deviations of approximation for the temperatures of 800, 850, and 900 $^\circ\text{C}$ are given in Table 4. From the values of the standard deviation

**Fig. 3.** Molar volume of the cross-sections of the quaternary system LiF—KF—B₂O₃—TiO₂ at 850 $^\circ\text{C}$. 1. LiF—KF—10 mole % B₂O₃ + 5 mole % TiO₂; 2. LiF—KF—20 mole % B₂O₃ + 5 mole % TiO₂.

of approximation it follows that the obtained equation satisfactorily describes the course of the molar volume in the investigated part of the quaternary system. The dependences of the molar volume of melts in the investigated cross-sections with the constant content of 5 mole % TiO₂ and with 10 and 20 mole % B₂O₃ are shown in Fig. 3. The value of the excess molar volume is again negative, but lower than without addition of TiO₂. For instance, the excess molar volume of the melt with the composition of 50 mole % KF, 25 mole % LiF, 20 mole % B₂O₃, and 5 mole % TiO₂ is $V_m(\text{ex}) = -2.07 \text{ cm}^3 \text{ mol}^{-1}$, which is 8.0 % of the value of the molar volume of this mixture. This effect is obviously connected with the formation of alkali metal titanates. Again the individual interaction terms may be ascribed to the chemical reaction of components.

REFERENCES

1. Makyta, M. and Matiašovský, K., to be published.
2. Chrenková, M. and Daněk, V., *Chem. Papers* 46, 167 (1992).
3. Chrenková, M. and Daněk, V., *Chem. Papers* 46, 222 (1992).
4. Janz, G. J., *Phys. Chem. Ref. Data* 17, 3 (1989).
5. Šilný, A., *Sdělovací technika* 38, 101 (1990).
6. Volf, M. B., *Skló ve výpočtech*. (Glass in Calculations.) P. 118. Nakladatelství technické literatury (Publishers of Technical Literature), Prague, 1984.

Translated by V. Daněk