Miscibility Gaps in Fused Salts
Note VIII. Mixtures Formed by LiF and two Alkali Bromides

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Demixing phenomena were studied in 12 mixtures type LiF + (Me_I, Me_{II}) Br, Me_I and Me_{II} being alkali metals. Previous measurements of the LL equilibria in the system LiF + CsBr were extended to the high temperature field to evaluate the position of the point of maximum. Moreover, the data obtained on the system LiF + NaBr were analyzed in order to calculate the critical temperature of the "submerged" gap. The results allowed to test the thermodynamic theories concerning the reciprocal ternary systems in the case of large deviations from ideality.

Note VII of this series [1] (cited from now on as VII) concerned demixing phenomena in the fused systems LiF + alkali halides. In particular, for the mixtures containing bromides, it was found that with NaBr no demixing is present and the main branch of the liquidus curve is "S' shaped, while the remaining three mixtures showed LL equilibria which could be completely measured only for the systems containing KBr and RbBr respectively.

In order to obtain more detailed information for the two mixtures containing NaBr and CsBr and thus to extend the possibility of testing the current thermodynamic theories on this type of systems (which are characterized by very large deviations from ideality), in the present paper demixing was studied in mixtures of LiF with pairs of alkali bromides.

For the system LiF + CsBr further measurements on the LL equilibria were also carried out which allowed to evaluate the position of the point of maximum (PM) of the miscibility gap (MG) even though the MG could not be completely studied.

Results and Discussion

Measurements of SL and LL equilibria were taken on the systems formed with LiF and mixtures of two bromides in the following molar ratios:

a) NaBr:KBr (2:3, 1:1, 3:1),
b) NaBr:RbBr (1:3, 1:1, 3:1),
c) NaBr:CsBr (1:1, 3:1, 9:1),
d) KBr:RbBr (1:1); KBr:CsBr (1:1); RbBr:CsBr (1:1).

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For the first three groups of systems detailed results are shown in Figures 1, 2. The extent of the gaps, in conformity with what found in VII, increases as the percentage of the larger cation increases.

Figure 2 also reports the MG of the pseudobinary LiF(1) + CsBr(2). This is an extension to the high temperature range of the measurements reported for this system in VII. Though the upper part of the gap could not be completed, these mea-

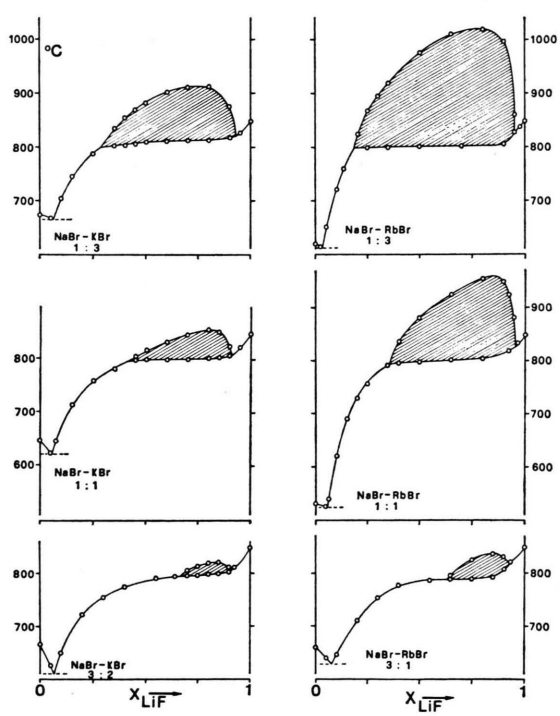

Fig. 1. Stratification areas (shaded) in a few sections of the mixtures LiF + NaBr + KBr and LiF + NaBr + RbBr.

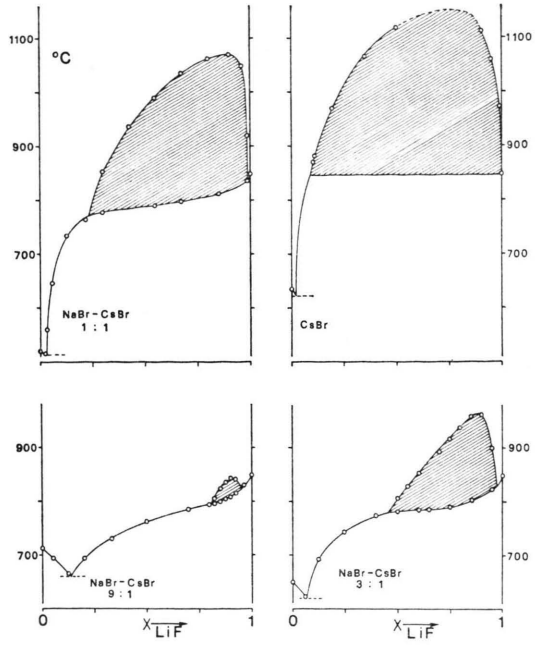

Fig. 2. Stratification areas (shaded) in a few sections of the mixture LiF + NaBr + CsBr.

surements allow to estimate the coordinates of the PM as $x_1 = 0.77$, $t = 1150$ °C.

The general topology of the systems LiF + NaBr + MeBr (Me = K, Rb, Cs) appears in the triangles of Fig. 3 where the projections of the studied cuts (dashed lines) and the temperatures corresponding to significant points of various type are reported. Data relative to the pseudobinary LiF + MeBr were taken from VII. The liquidus curve of the binary NaBr + KBr is continuous with a minimum at 644 °C and $x_{NaBr} = 0.52$, thus indicating the reciprocal mutual solubility of the two salts. Bellanca [2] and Ilyasov [3] had already studied this system with analogous results. The binary NaBr + RbBr shows a eutectic at 505 °C and $x_{NaBr} = 0.47$: Samuseva and Plyushchev [4] found a eutectic at 495 °C and $x_{NaBr} = 0.45$. Finally, the binary NaBr + CsBr shows a eutectic at 477 °C, $x_{NaBr} = 0.43$: these data can be compared with those reported by Ilyasov [5] (t = 482 °C, $x_{NaBr} = 0.43$ [graphically estimated]). In each case the demixing area impinges on the primary crystallization field of LiF starting from the pseudobinary LiF + MeBr (Me = K, Rb, Cs). Figure 3 also reports the projections of some LL isotherms.

The overall results for the temperatures t_{max} corresponding to the PM of the mixtures LiF +

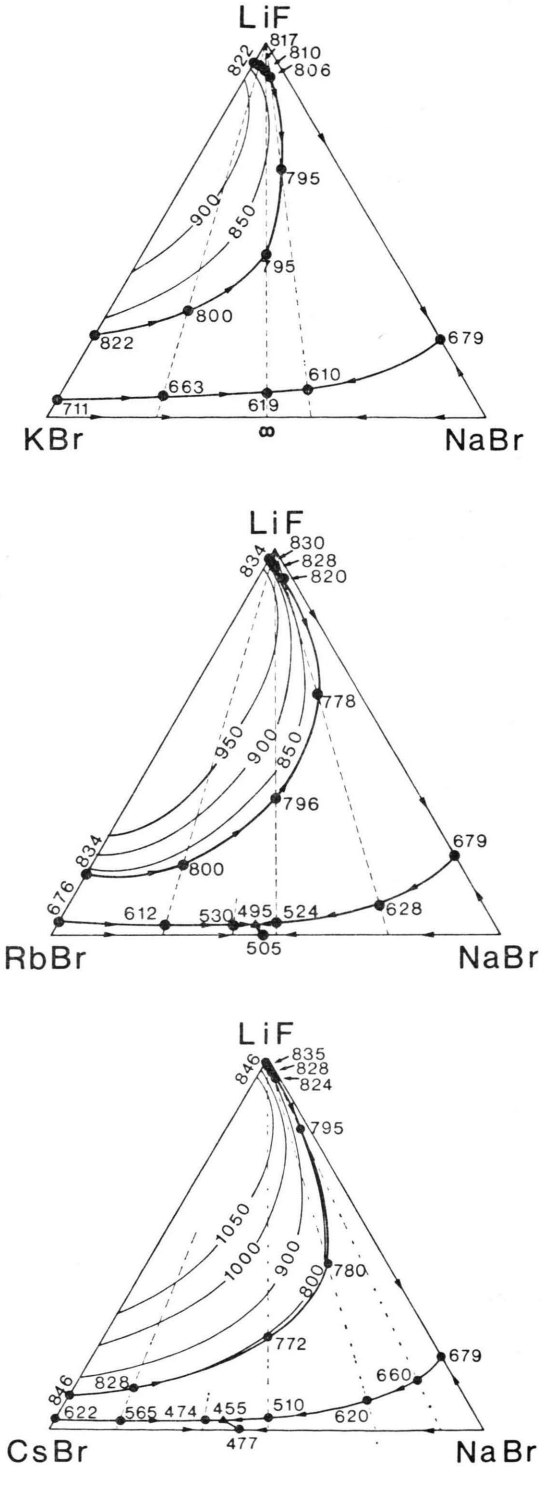

Fig. 3. Topology of the system: a) LiF + NaBr + KBr; b) LiF + NaBr + RbBr; c) LiF + NaBr + CsBr (along with the cuts of Fig. 2, two other sections, measured to complete the topology, are reported).

$(Me_I, Me_{II})Br$ are shown in Fig. 4 as a function of the concentration ratio of the two bromides.

The value of the critical temperature for the metastable "submerged MG" [6] in the system LiF(1) + NaBr(2) was estimated through the following procedure. On the basis of the SL equilibrium data reported in VII, the non-isothermal excess potentials $\mu_1^E(x_2)$ were obtained. The corresponding isothermal values were then evaluated at a fixed temperature (1000 K) within the experimental range: the temperature corrections, which are rather small, have been calculated using the Eqs. reported in VII. The derivative $d\mu_1^E/dx_2$ was then graphically evaluated at the critical point and finally used to obtain the critical temperature by means of the equation:

$$T_c = \frac{x_{1,c}}{2R}\left(\frac{d\mu_1^E}{dx_2}\right)_{\text{at } x_{2,c}}. \qquad (1)$$

Equation (1) follows from the condition $da_1/dx_1 = 0$ $(a_1 = \gamma_1 x_1^2)$. In the case of LiF + NaBr, assuming $x_{1,c} = 0.70$, Eq. (1) yields $t_c = 640\ ^\circ C$. This value, as well as that concerning the system LiF + CsBr $(t_c = 1150\ ^\circ C)$, is consistent with those measured

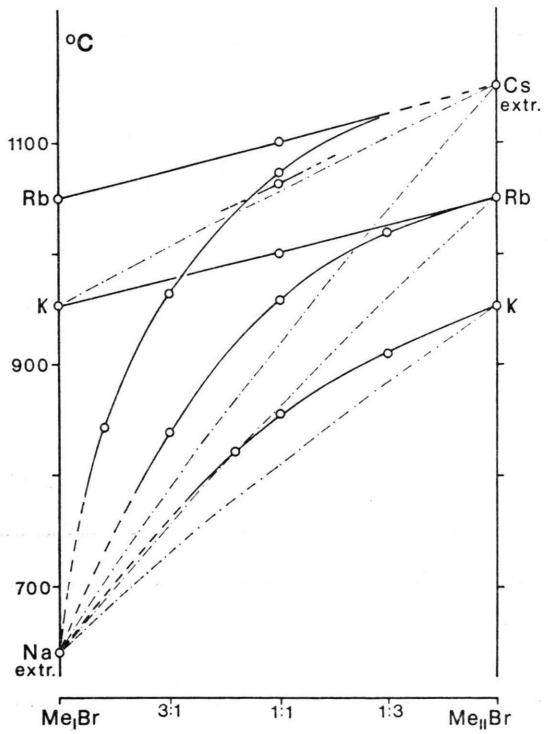

Fig. 4. Values of t_{max} in the mixtures LiF + $(Me_I, Me_{II})Br$ as a function of the concentration ratio of the two bromides. The dashed curves represent the energy additive behaviour.

for the mixtures containing two bromides (see Figure 4). The dashed curves which represent the additive behaviour of the mixtures with respect to the energy parameters also appear in Fig. 4 and will be discussed further on.

The choice $x_{1,c} = 0.70$ for the binary containing NaBr is due to the fact that a higher value of $x_{1,c}$ would exceed the one of the system containing KBr. Smaller values for $x_{1,c}$ give t_c s smaller than 640 °C which become less and less consistent with the data taken on the mixtures. On the basis of Fig. 4 it seems reasonable to fix the coordinates of the upper critical point of the system LiF + NaBr in the range: $x_{1,c} = 0.70 - 0.68$ corresponding to $t_c = 640 - 578\ ^\circ C$.

Now, the PM coordinates of the family LiF + MeBr being all available, it is possible to test more strictly the thermodynamic theories for the reciprocal ternary systems summarized in VII.

Assuming that the standard molar Gibbs free energy for the metathetical reaction, ΔG^0, can be written as

$$\Delta G^0 = \alpha + \beta T, \qquad (2)$$

Equation (1) gives the following results.

1) Using the ionic random arrangement model and taking into account only the first coordination sphere (cation-anion contacts) with Eq. (2-VII) the following value is obtained:

$$T_c^{R1} = \frac{\alpha}{(R/x_{1,c}\,x_{2,c}) - \beta}. \qquad (3)$$

2) Using the random model and taking into account also the interactions of the second coordination sphere (nearest ions of the same sign) with Eq. (4-VII) it is possible to evaluate the contribution to T_c given by the second shell as:

$$T_c^{R2} = \frac{x_{1,c}\,x_{2,c}}{R}\,[k' + (2 - 3x_2)(k'' - k')] \qquad (4)$$

where $k' = k_{Me} + k_X$ and $k'' = k_{Li} + k_F$.

3) To account for the non-random distribution of the ions in the first coordination shell, it is possible to use Blander's symmetric approximation. With Eqs. (5-VII) and (6-VII) one obtains:

$$T_c^{R1} + T_c^{NR} = \alpha \Big/ \left(Z R \ln \frac{\omega + 1}{\omega} - \beta\right) \qquad (5)$$

where $\omega = x_{1,c}\,x_{2,c}[(Z-2)^2/(Z-1)]$ and Z = coordination number. It is thus possible to obtain with

Eqs. (3), (4), (5):

$$T_c = T_c^{R1} + T_c^{R2} + T_c^{NR}. \quad (6)$$

4) Blander [7] has also suggested the following approximate equation (here written as a function of α and β):

$$T_c = \frac{\alpha}{5.5\,R - \beta} + \frac{k' + k''}{11\,R - 2\,\beta} \quad (7)$$

which can be obtained through the two following approximations:

$$x_{1,c} = x_{2,c} = 0.5 \quad \left(\therefore T_c^{R1} = \frac{\Delta G^0}{4\,R}\ ; \quad T_c^{R2} = \frac{k' + k''}{8\,R} \right) \quad (8)$$

and

$$T_c^{NR} = -0.375\,T_c. \quad (9)$$

Equation (9) is equivalent to the original Blander's approximation:

$$\Delta_c / R\,T_c = -3 \text{ (see Ref. [7])}.$$

The experimental data relative to the family LiF + MeBr were used in order to test Eqs. (3 – 7): the used parameters were those given by Lumsden [8]. Table 1 reports the studied pseudo-binaries, the position of the PM's, the values of T_c^{R1} [obtained by means of Eq. (3)], $T_c^{R1} + T_c^{R2}$ [Eqs. (3), (4)], $T_c^{R1} + T_c^{R2} + T_c^{NR}$ [Eq. (6) with $Z = 5$], and finally the T_c's obtained according to Equation (7). It is apparent from the table that, compared to the experimental data, the T_c^{R1} values are always too large, the values $T_c^{R1} + T_c^{R2}$ reproduce the experimental ones with a mean difference of $\pm 28°$, while the values $T_c^{R1} + T_c^{R2} + T_c^{NR}$ are always too small. The results obtained by Eq. (7) are unexpectedly good: the experimental values can be reproduced with a mean difference of $\pm 23°$ ($\pm 2\%$).

In consideration of the simplicity of this equation, and of the good results it gives, the upper consolute temperatures of the mixtures LiF + (Me_I, Me_{II})Br were calculated by Eq. (7) assuming the additivity of the energy parameters (ΔG^0, k', k''). Their behaviour is shown in Fig. 4 with dashed lines.

Me_I	Me_{II}	$-\Delta t$
Na	K	49
Na	Rb	96
Na	Cs	154
K	Rb	0
K	Cs	7
Rb	Cs	0

Table 2. Values of $\Delta t (\equiv t_{calc} - t_{exp})$ for the systems LiF + (Me_I, Me_{II})Br (1:1).

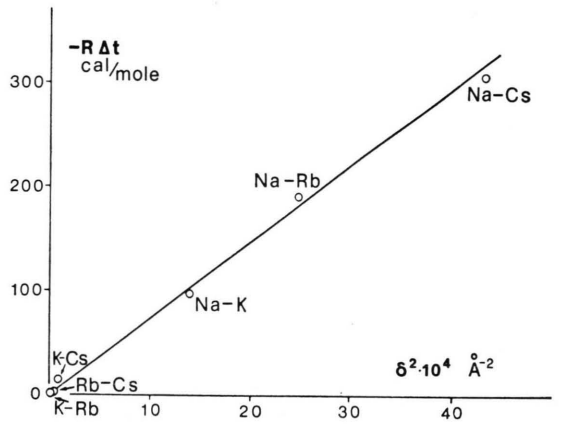

Fig. 5. Values of $-R\,\Delta t$ as a function of the δ^2 parameter.

For the mixtures having a 1:1 molar ratio of the two bromides, Table 2 reports values of $\Delta t = t_{calc} - t_{exp}$: they are null or negative. Data of $-R\,\Delta t$ plotted (see Fig. 5) as a function of the Reiss, Katz, and Kleppa parameter [9]

$$\delta^2 = [(d_1 - d_2)/(d_1\,d_2)]^2 \quad (10)$$

(d_1 = sum of the ionic radii of Me_IBr, d_2 = sum of the ionic radii of Me_{II}Br) give a good linear dependence. This was previously pointed out [10] also for the systems TlBr + (Me_I, Me_{II})NO_3 (1:1).

Table 1. Comparison of the T_c values as calculated by different equations. All the temperatures are in K; T_c^{NR} was calculated assuming $Z = 5$.

Systems	Coordinates of PM		T_c^{R1}	$T_c^{R1} + T_c^{R2}$	$T_c^{R1} + T_c^{R2} + T_c^{NR}$	T_c with Eq. (7)
LiF + NaBr	$x_{1,c} = 0.70$	$T_c = 913$	1144	893	725	894
LiF + KBr	$x_{1,c} = 0.70$	$T_c = 1226$	1691	1202	984	1233
LiF + RbBr	$x_{1,c} = 0.76$	$T_c = 1323$	1637	1266	1123	1340
LiF + CsBr	$x_{1,c} = 0.77$	$T_c = 1423$	1744	1432	1298	1470

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