Miscibility Gaps in Fused Salts. Note X.
The Reciprocal Ternary System K, Li/Br, F

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Solid-liquid and liquid-liquid equilibria in the reciprocal ternary system K, Li/Br, F were reported by Volkov
and Dubinskaya [1] in 1953, whereas the LL equilibria were studied only along the stable diagonal (LiF + KBr) and reported in Note VII of this series [2].

The present paper gives a complete experimental analysis of the SL and LL equilibria taking into account the full range of compositions and temperatures. Moreover, the results of the conformal ionic solution (CIS) theory [3] when applied to this system along with a discussion of the applicability limits of the theory are reported.

The apparatus, the experimental techniques and the characteristics of the employed salts were described in previous papers [4].

Results

Figure 1 shows the SL equilibria, along with the coordinates of the eutectics, of the four binaries.

Figure 2 reports the SL and LL equilibria along the unstable diagonal (KF + LiBr) and the stable one (LiF + KBr): the area in which demixing occurs is shaded.

As regards the unstable diagonal, the primary crystallization temperature (PCT) varies from 801 °C (x_{LiBr} = 0.41) to 798 °C (x_{LiBr} = 0.59) going through a maximum at 822 °C (x_{LiBr} = 0.50); the point of maximum of the miscibility gap is at 930 °C (x_{LiBr} = 0.50).

The stable diagonal was fully described in Reference [2].

The general topology of the system K, Li/Br, F is shown in Figure 3. Figure 3a reports the projection of the 12 studied cuts along with various significant temperatures. The stratification lens (dashed) impinges on the LiF crystallization field and occupies 20.8% of the square. The main axis of the lens coincides with the principal diagonal, and along this axis the PCT is constant at 822 °C. Figure 3b reports the projection of some LL isotherms: the upper critical point of the system is at 953 °C and x_{LiF} = 0.70; x_{KBr} = 0.30.

The system presents two ternary eutectics at 320 °C (x_{LiF} = 0.035; x_{LiBr} = 0.545; x_{KBr} = 0.42) and at 465 °C (x_{LiF} = 0.075; x_{KBr} = 0.605; x_{KF} = 0.32), respectively.

The comparison of the present results with the ones in Ref. [1] shows only a qualitative topological agreement, the numerical data being in some cases quite different. The invariant point E2, for instance, is reported in Ref. [1] as a peritectic point at 558 °C (x_{LiF} = 0.05; x_{KBr} = 0.545; x_{KF} = 0.395).

Discussion

Among the recent applications of the CIS theory the a priori prediction of the LL equilibria in the reciprocal ternary system Na, Ti/Br, NO3 [3] has been...
Fig. 1. Phase diagrams for the four binaries KF + KBr; KBr + LiBr; LiF + KF and LiBr + LiF.

Fig. 2. SL and LL equilibria for the stable and unstable diagonals. The area in which demixing occurs is shaded.

particularly successful. Since LL equilibria are only present in systems very far from ideal behavior, the applicability of the theory could be questionable.

In the CIS theory the excess potential of the $i$-th component can be written as

$$\mu_i^e = f_1(\Delta G^0) + f_2(k_j) + f_3(A),$$

where $f_1, f_2, f_3$ are different functions of the composition of the system. The first addendum in Eq. (1) is due to the interactions with the first coordination sphere and contains the standard molar Gibbs free energy change ($\Delta G^0$) for the metathetical reaction

$$\text{LiF} + \text{KBr} \rightarrow \text{LiBr} + \text{KF}.$$  

The second term in (1) is connected with the second coordination sphere and contains the four $k_j$ terms which are the interaction parameters of the four binary mixtures with common $j$-ion.

The third term contains a characteristic quantity ($A$) of the CIS theory. A detailed discussion on this term can be found in Ref. [3]: briefly it contains $\Delta G^0, k_j$ and the coordination number $Z$.

For the present system, the $\Delta G^0$ has been reported by Lumsden [5] as $\Delta G^0 = 20900 - 2.9 T$. The $k_j$ values can be calculated from the coordinates of the binary eutectics as suggested by Ref. [3]; the following results are obtained (for comparison data from Ref. [5] are also reported in parenthesis):

$$k_{Li} = -860 \quad (-900) \text{ cal mole}^{-1},$$
$$k_K = -180 \quad (0),$$
$$k_F = -4265 \quad (-4700 + 1.3 T),$$
$$k_{Br} = -3535 \quad (-3200).$$
On the basis of these data, and using $Z=6$, attempts were made to predict the LL equilibria by means of the CIS theory. The evaluation of the LL equilibria field was obtained by a computer study of the free energy of mixing. In a reciprocal ternary system one should study the molar free energy of mixing as a function of the square composition and find the plane which is double tangent to this surface. For systems like the present one, where tie-lines are practically parallel to the stable diagonal, the problem can be reduced to a two dimensional one by dividing the composition square into parallels to the stable diagonal. The computer application of the method of successive approximations along each of the parallels readily yields the two tangent contact points between the studied function and the double tangent straight line.

The results thus obtained bring into evidence that: a) the symmetry of the miscibility gap (MG) is incorrect: the calculated point of maximum along the stable diagonal (PM) is at $x_{LiF}=0.40$ and $t=1046^\circ C$ while the experimental one is at $x_{LiF}=0.70$ and $t=953^\circ C$; moreover the MG is too large along the unstable diagonal; b) a smaller $AG^0$ value ($19300 - 2.9 T$) lowers the PM but leaves the symmetry unchanged: the PM coordinates in this case are $x_{LiF}=0.40$ and $t=924^\circ C$.

Analogous results were obtained when the $k_j$'s by Ref. [5] were used.

Preliminary calculations carried out in order to test the influence of the different parameters showed that the symmetry and, to some extent, the width of the MG are strictly dependent on the $k_j$ values. The following regularities were observed:

a) a positive $k_j$ shifts the MG toward the stable pair component present in the common $j$-ion binary; moreover, the extension of the gap and the PM are largely increased;

b) a negative $k_j$ shows opposite effects, except it does not lower the PM of the MG;

c) the overall effect of the four $k_j$'s can be considered additive.

Owing to these results, a possible temperature dependence of $k_j$ was taken into account. In general $k_j$ is a function of temperature and composition; assuming that $k_j$ varies only with temperature, the experimental data relative to the liquidus curves of the four binaries give the following results:

$$k_{Li} = -3160 + 3.7 T, \quad k_F = -4265,$$
$$k_K = 60 - 0.8 T, \quad k_BT = -3535 . \quad (4)$$

The apparent dependence on temperature thus obtained is quite unexpected: it should be noted that this dependence was obtained using the LiF branch of the liquidus curve because of its wider temperature range.

The data (4), when used in connection with (1), yield an improvement in the prediction of the LL equilibria: The symmetry of the MG is qualitatively correct even if the shape is still somewhat different from the experimental one and too wide along the unstable diagonal. For instance, using $Z=6$ and $AG^0=19000 - 2.9 T$, the calculated PM is now at $x_{LiF}=0.65$ and $t=960^\circ C$. 

Fig. 3. a) Diagonal and offdiagonal cuts in the reciprocal ternary K, Li/Br, F with some significant temperatures. 

b) General topology of the ternary system with the projections of some isotherms: LL isotherms are dotted.
Conclusion

The results here obtained show the importance of the $k_j$ terms when used in the CIS theory. The assumption that $k_j$ is constant can lead (as in the present case) to an incorrect prediction of characteristics of the miscibility gap such as its symmetry.

Thus it seems possible to conclude that the CIS theory yields only semiquantitative predictions when applied to systems like the present one when the temperature dependence of $k_j$ is not taken into account.

Better results could probably be obtained by the extension of the theory to higher order terms and by taking into account the exact dependence of $k_j$ (and probably $Z$) on temperature and composition.


