Miscibility Gaps in Fused Salts. Note XII. Systems Formed with Thallium (I) Halides and Lithium or Sodium Halides: the Ternary Li, Tl/Cl, I

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Demixing was investigated in the molten salt families formed with thallium (I) halides and lithium or sodium halides. Measurements were carried out on the twelve stable diagonals of the corresponding reciprocal ternary mixtures. Liquid-liquid equilibria were found in the three systems TlCl + LiF, TlBr + LiF and TlI + LiCl while in the two systems formed with TlI and LiF or NaF measurements could not be carried out owing to the thermal instability of TlI.

The reciprocal ternary Li, Tl/Cl, I exhibits demixing in a temperature range which is convenient for investigation: therefore the whole composition square was studied. The upper critical solution point of the gap lies along the stable diagonal at 734 °C and $x_{LiCl} = 0.58$. The projection of the stratification lens occupies 38.8% of the composition square. Moreover an "a priori" prediction of the liquid-liquid equilibria was carried out by means of the conformal ionic solution-theory.

The present paper reports on the occurrence of demixing in melts formed with thallous halides and lithium or sodium halides. The stable diagonals of the relevant reciprocal ternaries were only taken into account: thus twelve mixtures (6 with the lithium ion and 6 with the sodium ion) were studied. Unfortunately, for LiF + TlI and NaF + TlI, the demixing expected could not be proved due to thermal instability of the thallium salts in the temperature range concerned. Previous literature reports only on the LiCl + TlBr [1] and NaCl + TlBr [2] systems, both of which do not exhibit liquid-liquid (LL) equilibria.

Research carried out on the eight remaining mixtures yielded the following results. The systems formed with LiF and TlCl or TlBr show immiscibility in the molten state, whilst the systems formed with NaF and TlCl or TlBr do not. Mixtures of TlI with LiBr, NaCl or NaBr present "S" shaped liquidus curves indicating a mere tendency to demix. Quantitative results on the first two systems are shown in Figure 1.

Finally, for LiCl + TlI a miscibility gap (MG) occurs in a temperature range suitable for full detection. Thus, it was thought proper to extend the study of the LL equilibria as a function of temperature to the whole composition square of the reciprocal ternary Li, Tl/Cl, I.

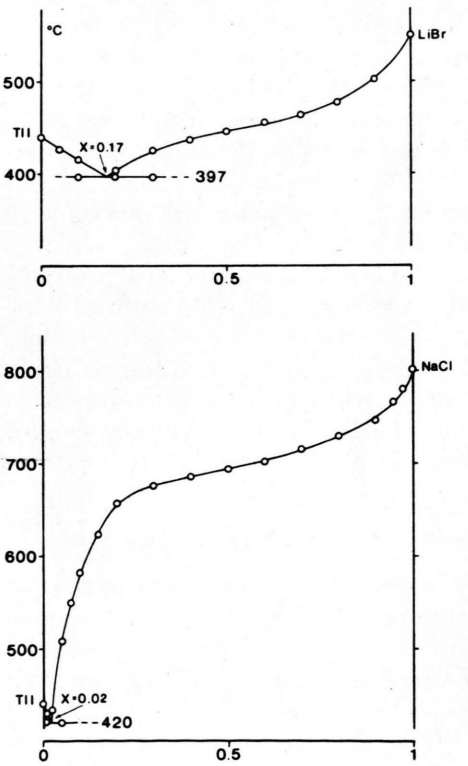

Fig. 1. Phase diagrams for the systems LiBr + TlI and NaCl + TlI.

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Table 1. Occurrence of LL equilibria in the salt family TlX + Li (or Na) Y (X, Y = F, Cl, Br, I) and ΔH^0 values relevant to the metathetical reactions in the molten state.

Stable pair	Demixing	ΔH^0/kcal mol^{-1}
TlI + LiF *	yes ?	29.0
TlI + LiCl	yes	11.5
TlI + LiBr	no	5.9
TlI + NaF *	?	15.0
TlI + NaCl	no	8.2
TlI + NaBr	no	4.3
TlBr + LiF *	yes	23.0
TlBr + LiCl	no	5.6
TlBr + NaF *	no	11.0
TlBr + NaCl	no	3.9
TlCl + LiF *	yes	17.0
TlCl + NaF *	no	7.0

* Based on the value $\bar{H}^{\circ}_{TlF} = -75$ kcal mol^{-1}: this was deduced taking $\Delta H^0_{f,298} = -77.8 \pm 1$ kcal mol^{-1} (see Ref. [7]), and assuming $\Delta H_F = 3$ kcal mol^{-1}.

Table 1 summarizes information about demixing for the twelve systems examined; the standard enthalpy changes, ΔH^0, of the corresponding metathetical reactions are also reported. The ΔH^0 values, calculated as previously indicated [3] on the basis of literature data [4–6], help to quantify the demixing tendency of a given system. The question marks denote the two mixtures that could not be investigated. At any rate the ΔH^0 values suggest occurrence of a MG to be likely for LiF + TlI, but doubtful for NaF + TlI due to the high melting point of NaF (995 °C).

The apparatus and the experimental procedure were described previously [8]. The salts used were: Merck suprapur Lithium and sodium halides; Fluka puriss. TlI. Moreover, Merck pro analysis $TlNO_3$ and Fluka puriss. KCl and KBr were employed to prepare TlCl and TlBr. Particular care was devoted to the drying of the lithium salts.

The Reciprocal Ternary System Li, Tl/Cl, I

Figure 2 shows the binary solid-liquid (SL) equilibria occurring along the sides of the composition square; the coordinates of the eutectics are also reported. Figure 3 shows the SL and LL equilibria along the stable and unstable diagonals (LiCl + TlI and LiI + TlCl, respectively): the demixing areas are shaded.

As regards the stable diagonal, the primary crystallization temperature (PCT) is constant at 580 °C from $x_{LiCl} = 0.07$ to $x_{LiCl} = 0.94$; in this

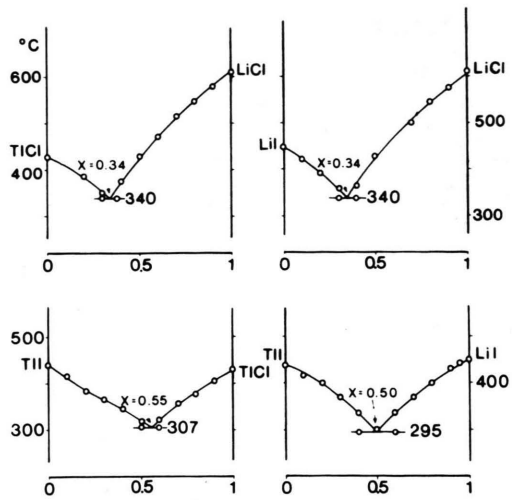

Fig. 2. Liquidus of the four binaries which are the sides of the composition square of the reciprocal ternary Li, Tl/Cl, I.

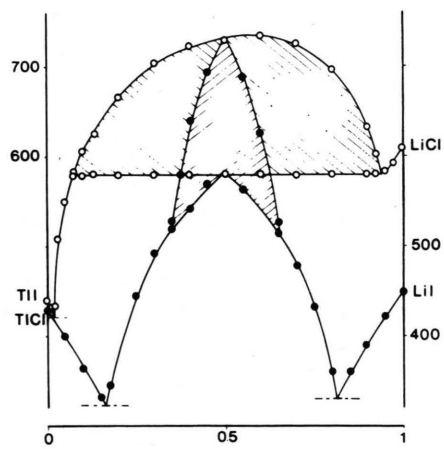

Fig. 3. SL and LL equilibria along the stable and unstable diagonals in the reciprocal ternary Li, Tl/Cl, I. Demixing areas are shaded.

pseudo binary the LL maximum is at $x_{LiCl} = 0.58$ and 734 °C, and the eutectic at $x_{LiCl} = 0.02$ and 423 °C.

As regards the unstable diagonal, the PCT varies from 517 °C ($x_{LiI} = 0.35$) to 515 °C ($x_{LiI} = 0.65$) going through a maximum at 580 °C ($x_{LiI} = 0.50$); the PM is at 732 °C ($x_{LiI} = 0.50$).

The LL and SL equilibria along the four most important off-diagonal cuts are reported in Figure 4. Cuts a) and b) were obtained by adding increasing amounts of LiI to mixtures of TlCl and TlI of starting compositions $x_{TlI} = 0.80$ and 0.50, respectively; cuts c) and d) by adding LiI to mixtures of TlCl

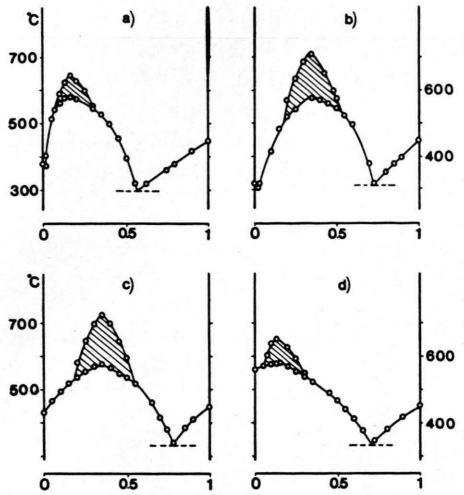

Fig. 4. SL and LL equilibria along the four (a–d) off-diagonal cuts studied. Demixing areas are shaded.

and LiCl of starting compositions $x_{LiCl} = 0.50$ and 0.85, respectively.

The topology of the system Li, Tl/Cl, I is shown in Figs. 5 a) and 5 b). Figure 5 a) reports the projection of the nine cuts examined, along with a number of significant temperatures. The stratification lens (dashed) impinges on the LiCl crystallization field, and occupies 38.8% of the composition square. The main axis of the lens and the principal diagonal overlap, the PCT being constant at 580 °C. Figure 5 b) reports the projections of some SL and LL isotherms: the upper critical point of the system coincides with the PM of the main diagonal. The system presents two ternary eutectics, E_1 at 290 °C ($x_{TlI} = 0.47_5$; $x_{LiI} = 0.48$; $x_{TlCl} = 0.04_5$) and E_2 at

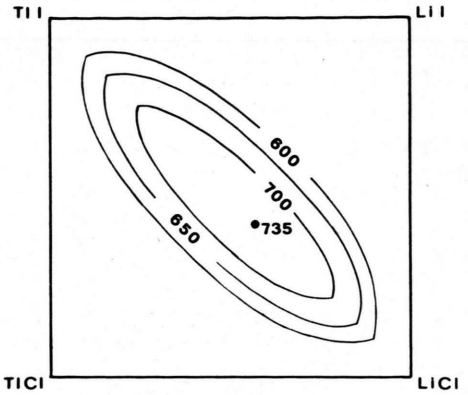

Fig. 6. LL isotherms as calculated by means of the CIS theory.

306 °C ($x_{TlI} = 0.46$; $x_{TlCl} = 0.51$; $x_{LiI} = 0.03$). This topology is compatible with the triangulation rules.

Finally an "a priori" prediction of the LL equilibria was carried out by means of the CIS theory [9]. As shown in previous papers [10, 11], calculations require the knowledge of the standard Gibbs free energy change, ΔG^0, for the metathetical reaction, of the four parameters, k, relevant to the binary mixtures, and of the coordination number Z. The first parameter has been deduced from the equation $\Delta G^0 = 11.5 - 0.0008\,T$ kcal mol^{-1}, which is compatible both with the data of Table 1 and with the relation suggested by Lumsden for the double decomposition of the alkali halides [5]. Moreover, Lumsden reported k (LiCl + TlCl) = −1.4 and k (TlCl + TlI) = 0.8 kcal mol^{-1} [5], while in a previous paper [3] we took k (LiCl + LiI) = 1.0 kcal · mol^{-1}. For k (LiI + TlI) the value −1.5 kcal mol^{-1}

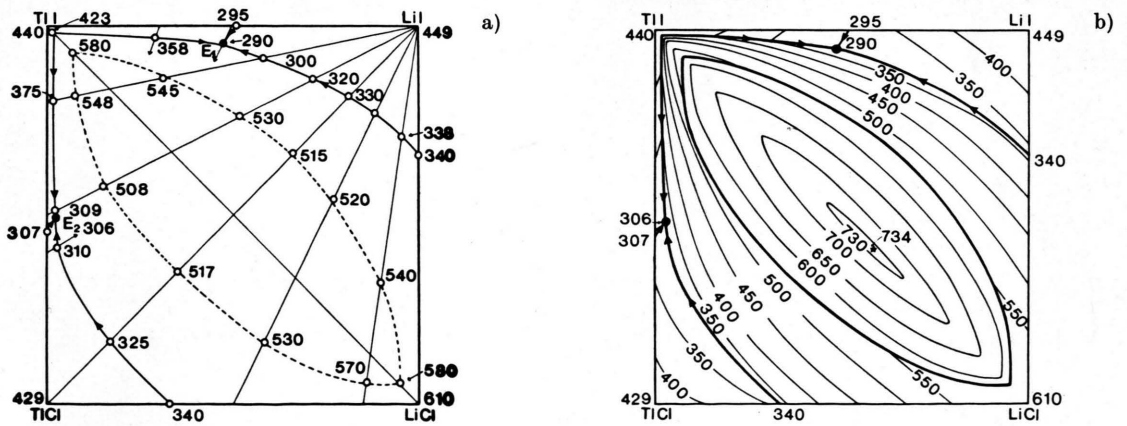

Fig. 5. a) Diagonal and offdiagonal cuts studied in the reciprocal ternary Li, Tl/Cl, I, along with some significant temperatures. b) General topology of the ternary system, along with the projections of some isotherms and of the MG lens.

was assumed here together with $Z = 6$. It should be noted that the four binary systems which represent the sides of the composition square are very likely affected by solid solutions; thus the method of the coordinates of the binary eutectics suggested in [9] cannot be used.

The results of the calculations based on the above set of data are summarized in Figure 6. The upper critical point was calculated at $x_{LiCl} = 0.57$, $x_{TlI} = 0.43$ and 735 °C, in fair agreement with the experiment. Also the LL isotherms calculated simulate, satisfactorily, the trend of the experimental data.

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