

# Miscibility Gaps in Fused Salts. Note XI.

## Systems Formed with Silver Halides and Lithium or Sodium Halides

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The salt families formed with silver halides and lithium or sodium halides were studied in order to investigate demixing in the liquid state. In particular, measurements were carried out on the stable diagonals of the 12 pertinent reciprocal ternaries. Liquid-liquid equilibria were found to occur in the 10 mixtures containing LiF, NaF, LiCl, LiBr and NaCl (the last one only in the presence of AgI).

The miscibility gap, however, could be fully measured only on the four mixtures AgBr + LiCl, AgI + LiCl, AgI + LiBr and AgI + NaCl; for these and for the mixture AgI + NaBr an "a priori" prediction of the gap was possible on the basis of current thermodynamic theories.

The systematic analysis of demixing in mixtures of fused salts is continued with the present paper which reports on the families formed with silver halides and lithium or sodium halides.

In each of the two groups of reciprocal ternaries  $\text{AgX} + \text{LiY}$  and  $\text{AgX} + \text{NaY}$  ( $\text{X}, \text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ), 4 binaries with a common ion, 6 unstable diagonals (e.g.  $\text{AgF} + \text{LiCl}$ ) and 6 stable diagonals (e.g.,  $\text{LiF} + \text{AgCl}$ ) are involved. The occurrence of demixing was detected for the 6 stable diagonals of the systems containing lithium ion and for 3 out of the 6 stable diagonals of the systems containing sodium ion (namely those containing AgI): liquid-liquid equilibria were found in eight out of these nine systems.

In order to complete information, a qualitative study was carried out also on the three remaining mixtures containing sodium ion: demixing was observed in  $\text{AgBr} + \text{NaF}$  and  $\text{AgCl} + \text{NaF}$ , but not in  $\text{AgBr} + \text{NaCl}$ .

Previous literature reported the occurrence of a miscibility gap (MG) only for the reciprocal ternary Ag, Li/Br, Cl [1], although no liquid-liquid (LL) equilibria were specifically measured and the miscibility limits were deduced only on the basis of the solid-liquid (SL) curves. Recently, detailed data on the reciprocal ternary Ag, Li/Br, I were published by our group [2].

### Apparatus and Materials

The apparatus and the experimental technique (based on the direct visual observation of the sample, possibly supported by DTA measurements) were described in previous papers of this series [3].

The salts used were Merck Suprapur lithium and sodium halides and Fluka puriss. AgF; moreover Fluka puriss.  $\text{AgNO}_3$ , KCl and KBr were employed to prepare AgCl and AgBr.

A particular care was taken in drying the lithium salts, following procedures suggested in the literature [4]. Moreover, for the system containing NaF (m.p.  $995^\circ\text{C}$ ) the occurrence of demixing was also investigated by a Leitz "Hot Stage" microscope: the melted mixtures were contained between two small disks of sapphire.

### Results and Discussion

The SL and LL equilibria in the six pseudo-binaries containing lithium ion are reported in Fig. 1, while those relevant to the three systems containing sodium ion are reported in Fig. 2: the demixing areas are shown by shading and the eutectic temperatures are also indicated.

The MG's could be fully examined in only four systems in as much as those found in mixtures containing LiF or NaF occurred at temperatures so high that only the primary crystallization temperature (PCT) could be measured accurately.

In the  $\text{AgX} + \text{LiY}$  family (see Fig. 1), when LiF is present, the MG extends almost to both the pure

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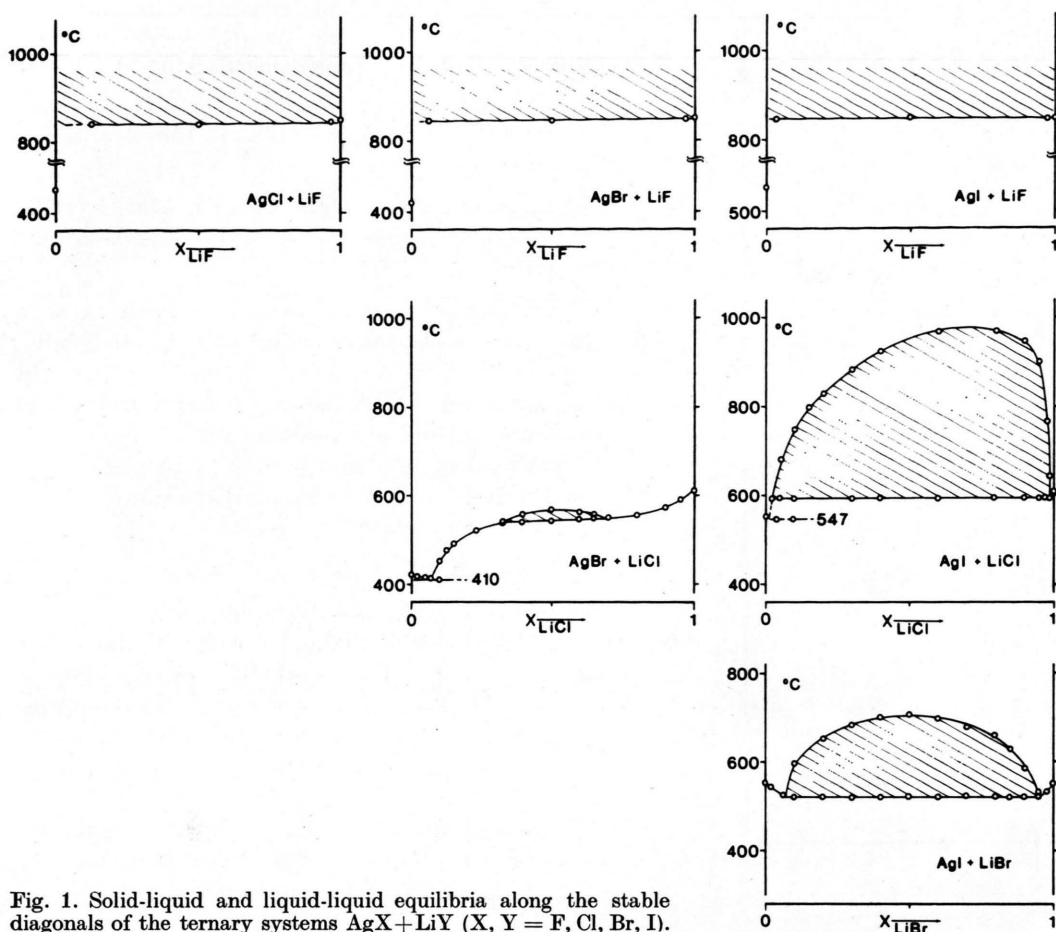


Fig. 1. Solid-liquid and liquid-liquid equilibria along the stable diagonals of the ternary systems  $\text{AgX} + \text{LiY}$  ( $X, Y = \text{F, Cl, Br, I}$ ).

components; the PCT's are constant at  $840^\circ$ ,  $845^\circ$  and  $847^\circ\text{C}$  for  $\text{AgCl} + \text{LiF}$ ,  $\text{AgBr} + \text{LiF}$  and  $\text{AgI} + \text{LiF}$  respectively (m.p. of  $\text{LiF}$ :  $848^\circ\text{C}$ ).

Also the two systems containing  $\text{LiCl}$  exhibit LL equilibria. In particular, in the system  $\text{AgBr} + \text{LiCl}$  a very small MG occurs: the PCT varies from  $540^\circ\text{C}$  (at  $x_{\text{LiCl}} = 0.32$ ) to  $548^\circ\text{C}$  (at  $x_{\text{LiCl}} = 0.70_5$ ). The complete MG was measured and the coordinates of the point of maximum (PM) were found to be  $x_{\text{LiCl}} = 0.52$  and  $t = 570^\circ\text{C}$ , the eutectic point was at  $x_{\text{LiCl}} = 0.07$  and  $t = 410^\circ\text{C}$ . Bergman and Arabadzhian [1] reported for the width of the MG the limiting values  $x_{\text{LiCl}} = 0.07_5$  (at about  $420^\circ\text{C}$ ) and  $x_{\text{LiCl}} = 0.68_5$  (at  $546^\circ\text{C}$ ), which are in disagreement with the present ones.

The system  $\text{AgI} + \text{LiCl}$  presents a very wide MG: the PCT is constant at  $594^\circ\text{C}$ , the limiting  $x_{\text{LiCl}}$  values being  $0.0_5$  and  $0.99$ . The MG was fully in-

vestigated and the coordinates of the PM were found to be:  $x_{\text{LiCl}} = 0.70$  and  $t = 976^\circ\text{C}$ ; the eutectic point was close to pure  $\text{AgI}$  at  $547^\circ\text{C}$ .

The only system containing  $\text{LiBr}$  (i.e.  $\text{AgI} + \text{LiBr}$ ) shows a medium-sized MG which was completely observed. For this system the PCT is constant at  $520^\circ\text{C}$ , for  $0.07 \leq x_{\text{LiBr}} \leq 0.95_5$ . The coordinates of the PM, which is also the upper critical solution point [2], are:  $x_{\text{LiBr}} = 0.50$  and  $t = 706^\circ\text{C}$ .

In the  $\text{AgX} + \text{NaY}$  family all of the three mixtures containing  $\text{NaF}$  show LL equilibria. Only  $\text{AgI} + \text{NaF}$ , however, could be studied quantitatively. In this system demixing extends almost from pure to pure component, with a constant PCT at  $989^\circ\text{C}$  (m.p. of  $\text{NaF}$ :  $995^\circ\text{C}$ ) (see Figure 2).

The system  $\text{AgI} + \text{NaCl}$  shows a small MG: PCT is constant at  $760^\circ\text{C}$  for  $0.20 \leq x_{\text{NaCl}} \leq 0.80$ . The MG was fully measured and the PM found at  $x_{\text{NaCl}}$

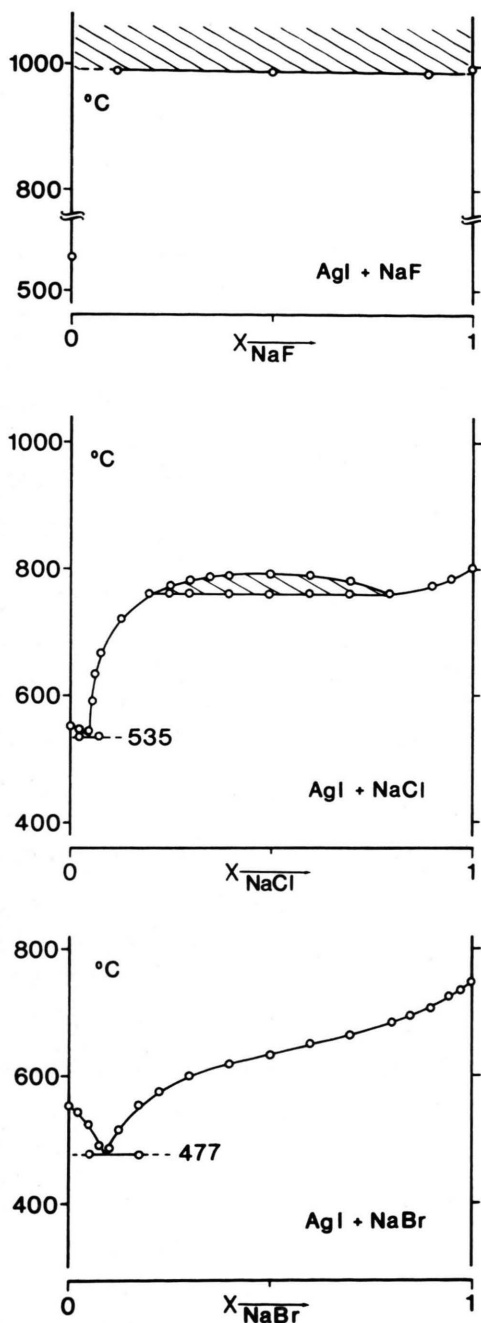


Fig. 2. Solid-liquid and liquid-liquid equilibria along the stable diagonals of the ternary systems  $\text{AgI} + \text{NaY}$  ( $\text{Y} = \text{F}, \text{Cl}, \text{Br}$ ).

$= 0.50$  and  $t = 793^\circ\text{C}$ . The eutectic coordinates are  $t = 535^\circ\text{C}$  and  $x_{\text{NaCl}} = 0.05$ .

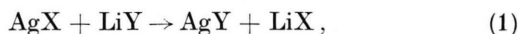
The system  $\text{AgI} + \text{NaBr}$  exhibits only an "S" shaped SL curve, indicating a "tendency" to demix. The eutectic is at  $477^\circ\text{C}$  and  $x_{\text{NaBr}} = 0.09$ .

From Figs. 1 and 2 one can see that the tendency to demix in these families increases:

- when, the alkali halide being the same (horizontal series), the anionic radius of the silver halide increases;
- when, the silver halide being the same (vertical series), the anionic radius of the alkali halide decreases.

Although these regularities are in agreement with the "reciprocal coulomb effect" (if the  $\text{Ag}^+$  radius is larger than the  $\text{Na}^+$  one), it seems likely that, the  $\text{Ag}^+$  ion being present, the ionic polarizabilities exert a paramount influence on demixing.

The tendency to demix in these systems correlates qualitatively with the standard enthalpy change,  $\Delta H^\circ$ , for the metathetical reaction:



where  $\text{AgX} + \text{LiY}$  is the stable pair.

In order to estimate the  $\Delta H^\circ$  values in the molten state, one can use the enthalpies of formation at 298 K of the components corrected with the proper enthalpies of transition and fusion. Table 1 lists the  $\Delta H^\circ$ 's obtained on the basis of the literature data [5, 6, 7].

An "a priori" prediction of the LL equilibria is possible by using the CIS theory developed by Blander *et al.* [8] and summarized (for the case of mixtures of the present type) in a previous paper [3]. Calculations require the availability of the standard Gibbs free energy change,  $\Delta G^\circ$ , for the metathetical reaction (1), the interaction parameters,  $k$ , pertinent to the four binaries, and the coordination number,  $Z$ . In order to obtain the  $\Delta G^\circ$ 's, the  $\Delta H^\circ$ 's of Table 1 and the empirical relation suggested by Lumsden [6], for the evaluation of  $\Delta S^\circ$  in the double decomposition of the alkali halides, were employed. Using the literature  $k$  values, when available, and the coordination number  $Z = 6$  (see Ref. 3), at-

Table 1.  $\Delta H^\circ$  values ( $\text{kcal mol}^{-1}$ ) for the metathetical reaction (1) in the molten state.

Stable pair	$\Delta H^\circ$	Stable pair	$\Delta H^\circ$
$\text{AgCl} + \text{LiF}$	29.6	$\text{AgCl} + \text{NaF}$	19.1
$\text{AgBr} + \text{LiF}$	37.4	$\text{AgBr} + \text{NaF}$	25.3
$\text{AgI} + \text{LiF}$	45.2	$\text{AgI} + \text{NaF}$	31.5
$\text{AgBr} + \text{LiCl}$	7.8	$\text{AgBr} + \text{NaCl}$	6.2
$\text{AgI} + \text{LiCl}$	15.6	$\text{AgI} + \text{NaCl}$	12.3
$\text{AgI} + \text{LiBr}$	7.8	$\text{AgI} + \text{NaBr}$	6.2

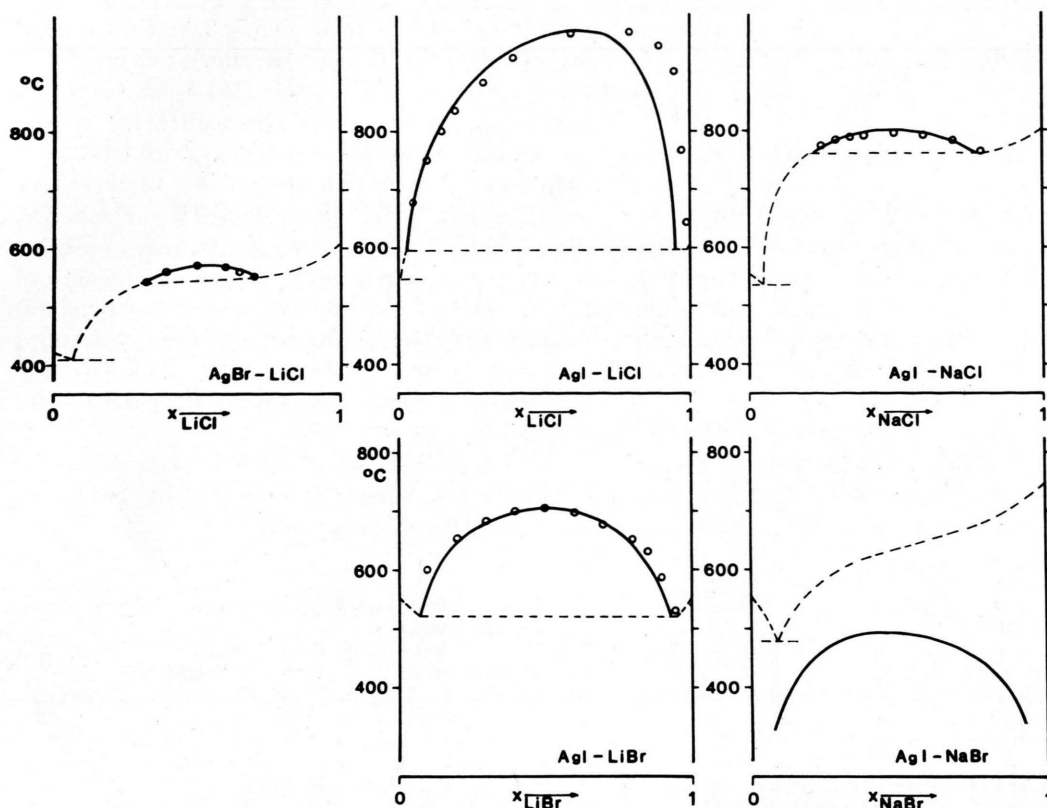


Fig. 3. Calculated liquid-liquid equilibria along the stable diagonals of the ternary systems  $\text{AgX} + \text{LiY}$  ( $\text{X}, \text{Y} = \text{Cl}, \text{Br}, \text{I}$ ) and  $\text{AgI} + \text{NaY}$  ( $\text{Y} = \text{Cl}, \text{Br}$ ).

tempts were made to predict the shape and location of the LL fields in the five mixtures of Figs. 1 and 2 which had been studied completely. The following results were obtained ( $\Delta G^\circ$  and  $k$  in  $\text{kcal mol}^{-1}$ ).

$\text{AgBr} + \text{LiCl}$ :  $\Delta G^\circ = 7.8 - 0.001(\pm 0.001)\text{T}$  (from Table 1);

$k(\text{AgCl} + \text{LiCl}) = 2.1$  and  $k(\text{AgBr} + \text{LiBr}) = 1.8$  (from [6]). In order to obtain a satisfactory picture of the system, however, one must use an about 10% smaller  $\Delta G^\circ$  value: this is a feature common to several systems studied in the present and previous works [9]. The results shown in Fig. 3 were obtained with  $\Delta G^\circ = 7.1 - 0.002\text{T}$  and assuming

$$k(\text{AgBr} + \text{AgCl}) = k(\text{LiBr} + \text{LiCl}) = 1.0,$$

which allowed the calculated PM to coincide with the experimental one.

$\text{AgI} + \text{LiCl}$ :  $\Delta G^\circ = 15.6 - 0.002(\pm 0.001)\text{T}$  (from Table 1);

$k(\text{AgCl} + \text{LiCl}) = 2.1$  and  $k(\text{AgCl} + \text{AgI}) = 0.45$  (from [10]). Also in this case the  $\Delta G^\circ$  value from Table 1 was too large. The results reported in Fig. 3

were obtained using  $\Delta G^\circ = 14.6 - 0.004\text{T}$  and assuming  $k(\text{AgI} + \text{LiI}) = k(\text{LiCl} + \text{LiI}) = 1.0$ . The PM coordinates thus calculated ( $x_{\text{LiCl}} = 0.66$  and  $t = 971^\circ\text{C}$ ) can be favourably compared with the experimental ones ( $x_{\text{LiCl}} = 0.70$  and  $t = 976^\circ\text{C}$ ). The MG calculated is more symmetrical (with respect to  $x = 0.5$ ) than the experimental one: the calculations could be improved using  $\text{T}$  (or composition) dependent  $k$  values so that, at high temperature (or in the composition range close to pure  $\text{LiCl}$ ) the  $k$  value of  $\text{LiCl} + \text{LiI}$  would be larger than that of  $\text{AgI} + \text{LiI}$  or the  $k$  value of  $\text{AgCl} + \text{LiCl}$  would be even larger than that of  $\text{AgCl} + \text{AgI}$ .

$\text{AgI} + \text{LiBr}$ : from Table 1:

$$\Delta G^\circ = 7.8 - 0.001(\pm 0.001)\text{T};$$

from the literature  $k(\text{AgBr} + \text{LiBr}) = 1.8$  and  $k(\text{AgBr} + \text{AgI}) = 1.1$  [10]. Assuming that the  $k$  values in this system are symmetrical [2] (i.e.  $k(\text{AgI} + \text{LiI}) = 1.8$  and  $k(\text{LiBr} + \text{LiI}) = 1.1$ ) one obtains the results reported in Figure 3. The cal-



culated MG presents the PM at  $x_{\text{LiBr}} = 0.50$  and  $t = 703^\circ\text{C}$  (experimental:  $x_{\text{LiBr}} = 0.50$  and  $t = 706^\circ\text{C}$ ) and at the lower temperatures is slightly smaller than the experimental one.

AgI + NaCl:  $\Delta G^\circ = 12.3 - 0.002(\pm 0.001)\text{T}$  (from Table 1);

$k(\text{AgCl} + \text{AgI}) = 0.45$ ,  $k(\text{AgCl} + \text{NaCl}) = 1.0$  from Ref. [11] and  $k(\text{NaCl} + \text{NaI}) = 0.7$  from [6]. The  $\Delta G^\circ$  value from Table 1 seems to be about 10% too large. Using  $\Delta G^\circ = 11.25 - 0.002\text{T}$ , and assuming  $k(\text{AgI} + \text{NaI}) = 1.2$  the results reported in Fig. 3 are obtained: the calculated PM coincides with the experimental one.

AgI + NaBr:  $\Delta G^\circ = 6.2 - 0.001(\pm 0.0005)\text{T}$  from Table 1;  $k(\text{AgBr} + \text{NaBr}) = 1.0$  from Ref. [6] and  $k(\text{AgBr} + \text{AgI}) = 1.1$  from Ref. [10]. Assuming  $k(\text{NaBr} + \text{NaI}) = 1.0$  and  $k(\text{AgI} + \text{NaI}) = 1.2$

one obtains the results of Figure 3. In this case the MG calculated is "submerged", i.e. it remains below the liquidus. The PM calculated is at  $t = 490^\circ\text{C}$  and  $x_{\text{NaBr}} = 0.47$ : at this composition the experimental SL equilibrium point is at  $t = 632^\circ\text{C}$ .

In conclusion, the general results of these calculations can be easily evidenced by comparing Fig. 3 with the corresponding systems in Figs. 1 and 2. It is apparent that, although the choice of the parameters (and in particular of the  $k$  values) is somewhat arbitrary, the results are satisfactory, at least topologically. It should be noted that the  $k$ 's are assumed as independent of temperature and composition.

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