Miscibility Gaps in Fused Salts

Note IV. Systems of Silver Halides with Alkali Molybdates *

CESARE SINISTRI, GIORGIO FLOR, and PAOLO FERLONI

Institute of Physical Chemistry, University of Pavia, Italy

(Z. Naturforsch. **23 a**, 2073—2076 [1968]; received 2 September 1968)

Molten mixtures of AgCl, AgBr and AgI with alkali molibdates have been investigated. The silver chloride presents stratification phenomena only with Li_2MoO_4, the silver bromide demixes with Li_2MoO_4 and Na_2MoO_4 while the silver iodide demixes with Li_2MoO_4, Na_2MoO_4 and K_2MoO_4. The ability of demixing, for mixtures containing the same halide, increases as the radius of the alkali cation diminishes (or the polarizing power of the same increases).

Moreover the whole composition square of the ternary reciprocal system Ag, Na/Br, MoO_4 has been investigated.

The present work reports the results obtained by a research undertaken to determine the existence of demixing phenomena in reciprocal ternary systems type Ag, Me/X, MoO_4 (Me = alkali cation, X = Cl, Br, I). With this aim in view, we have investigated in a systematic manner the presence of miscibility gaps in the mixtures $AgX + Me_2MoO_4$ which are the stable diagonals of the corresponding reciprocal ternary systems. For the $AgBr + Na_2MoO_4$ system the research has also been extended to the whole compositon square.

Previously BELYAEV[1] found the existence of a miscibility gap (MG) in the systems $AgCl + Na_2MoO_4$, $AgBr + Li_2MoO_4$ and $AgBr + Na_2MoO_4$. These data will be discussed later. The demixing phenomena in the system Ag,Li/Cl,MoO_4 have been studied by LESNYKH and BERGMAN[2].

Apparatus and Materials

The apparatus employed has already been described[3]. Because of the high temperatures, quartz test-vessels were necessary: unfortunately the vessels became opaque after one or two determinations (particularly with lithium salts) and thus had to be changed frequently.

The salts used were: AgCl, AgBr and AgI freshly prepared by precipitation from an aqueous solution of $AgNO_3$ (C. Erba RP); Li_2MoO_4 (Alfa Inorganics Inc.); Na_2MoO_4 and K_2MoO_4 (BDH Analar). The rubidium molibdate was prepared by fusion starting from Rb_2CO_3 and MoO_3 (C. Erba RP). The melting point of this product was 955 °C while in literature we have found the values 944 °C[4] and 958 °C[5]. Finally the silver molibdate was an Alfa Inorganics Inc. product. The melting piont found for this salt was 571 °C, while in literature the values 554 °C[6] and 483 °C[7] are reported. To control, a sample of Ag_2MoO_4 was prepared according to MCCAY[8]. The m.p. of this sample, measured in a quartz test-vessel using the visual method, reconfirmed the value of 571 °C. In addition we have also made a X-rays powder spectrogram of the same sample: this was identic to those reported by the ASTM cards.

Results and Discussion

a) Mixtures $(AgX)_2 + Me_2MoO_4$

Fig. 1 reports the solid-liquid (SL) and liquid-liquid (LL) equilibria in the mixtures $(AgX)_2 + Me_2MoO_4$ (X = Cl, Br, I; Me = Li, Na, K) and $(AgI)_2 + Rb_2MoO_4$. The demixing area has been shaded.

As regards the systems containing AgCl, demixing occurs only in the mixture $(AgCl)_2 + Li_2MoO_4$.

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* Work carried out with the financial aid of the Consiglio Nazionale delle Ricerche, Rome.

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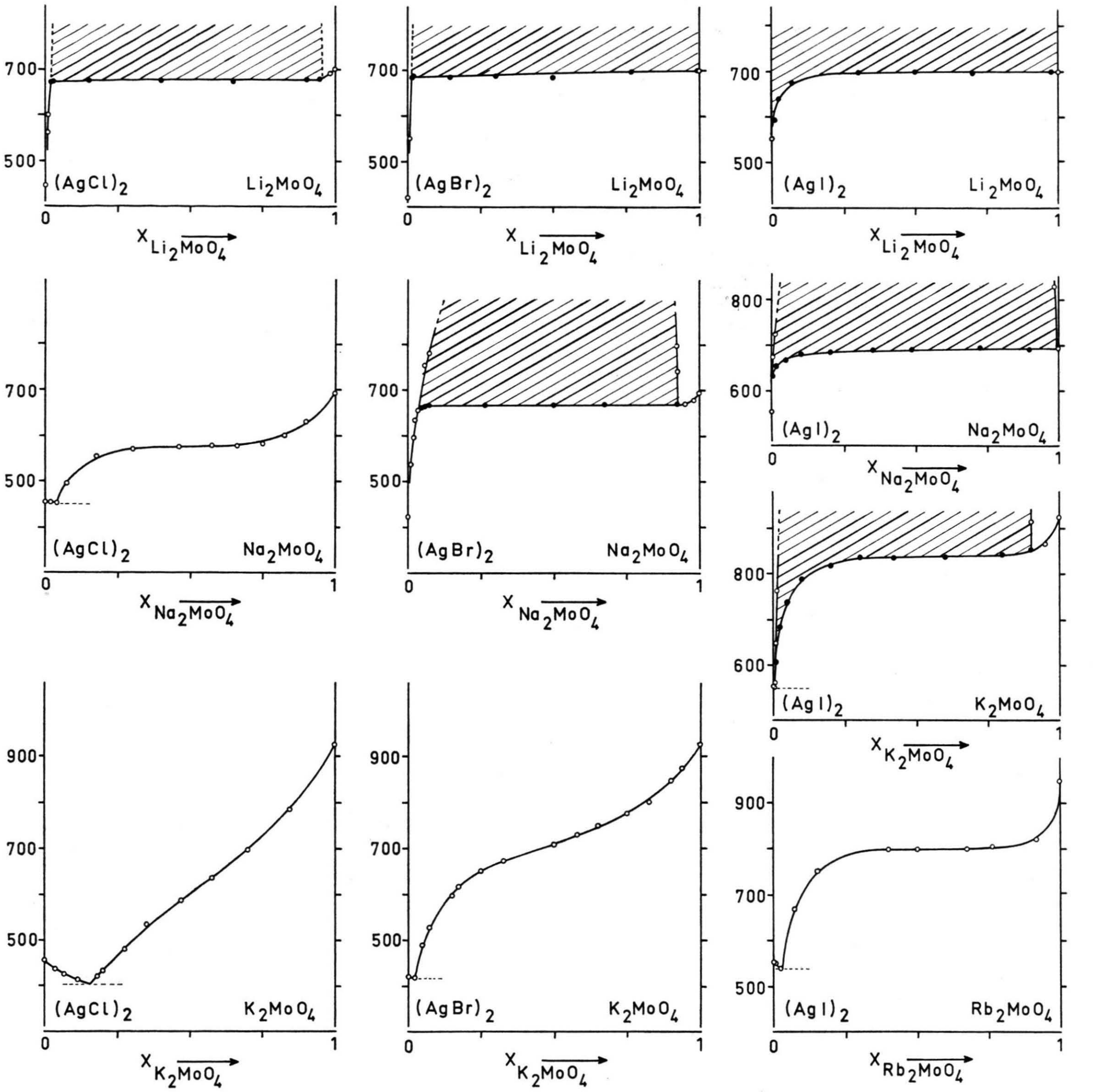

Fig. 1. Mixtures of silver chloride, bromide and iodide with alkali molibdates. The little circles represent SL or LL equilibria while the black points represent primary cristallization temperatures. The m. p. of the pure salts are: AgCl 456°, AgBr 421°, AgI 553°, Li_2MoO_4 700°, Na_2MoO_4 693°, K_2MoO_4 926° and Rb_2MoO_4 955 °C.

For this system, the primary cristallization temperature (PCT) from one of the two liquid phases in equilibrium, slightly increases from 674 °C to 678 °C when $x_{Li2MoO4}$ increases from 0.01_5 to 0.96_5. For the system $(AgCl)_2 + Na_2MoO_4$ demixing was not found but only a liquidus curve clearly "S" shaped, which proofs a great tendency to split into two liquid phases. The eutectic is at 454 °C and $x_{Na2MoO4} = 0.05$. On the contrary Belyaev[1] reports for this system a liquid miscibility gap extending from 87.5 to 50 AgCl mole% at the constant monotectic temperature of 550 °C. The $(AgCl)_2 + K_2MoO_4$ system shows a simple eutectic at 401 °C and $x_{K2MoO4} = 0.15$.

As regards the systems containing AgBr, demixing occurs in the two mixures with Li_2MoO_4 and Na_2MoO_4. In the $(AgBr)_2 + Li_2MoO_4$ system demixing extends from almost pure AgBr to almost pure Li_2MoO_4 whereas the PCT increases from 684 to 700 °C. Belyaev[1] found for this system a constant PCT at 670 °C and a MG extending from 98.5 to 2.5 AgBr mole %. The $(AgBr)_2 + Na_2MoO_4$ system will be discussed later. The $(AgBr)_2 + K_2MoO_4$ system shows a liquidus curve weakly "S" shaped with a eutectic at 418 °C and $x_{K2MoO4} = 0.02_5$.

As regards the systems containing AgI demixing occurs in the three mixtures with Li_2MoO_4, Na_2MoO_4 and K_2MoO_4. In these systems the PCT is a sensible function of the composition and presents a characteristic behaviour in the proximity of pure AgI as shown in Fig. 1. In the $(AgI)_2 + Li_2MoO_4$ mixture the MG extends from almost pure AgI to almost pure Li_2MoO_4 whereas the PCT increases from about 553° to 700 °C. In the $(AgI)_2 + Na_2MoO_4$ system the MG extends from almost pure AgI to almost pure Na_2MoO_4, whereas the PCT increases from about 625° to 692 °C. In the $(AgI)_2 + K_2MoO_4$ system the PCT increases from 630° ($x_{K2MoO4} = 0.01$) to 856 °C ($x_{K2MoO4} = 0.90_5$).

In the mixtures containing AgCl with each of the alkali molibdates, demixing is already prevented when the halide is coupled with Na_2MoO_4. In the case of AgBr, demixing is prevented only when the halide is coupled with K_2MoO_4. In the case of AgI even the K_2MoO_4 does not extinguish the MG. This is why we studied the mixture with the rubidium salt. The state diagram $(AgI)_2 + Rb_2MoO_4$, which appears in Fig. 1, presents a liquidus curve clearly "S" shaped and no demixing phenomenon. This system has a eutectic at 539 °C and $x_{Rb2MoO4} = 0.03_5$.

Fig. 1 shows that in this family the tendency to demix increases as the radius of the alkali cation diminishes (or as the polarising power of the same increases) for mixtures containing the same silver halide, whereas in those mixtures with the same alkali molibdate this tendency increases when silver chloride, bromide and iodide are successively taken as AgX. This is in agreement with what we had previously observed [3, 9, 10].

b) The system $Ag,Na/Br,MoO_4$

Fig. 2 shows the SL equilibria relative to the four binary systems constituting the sides of the composition square.

The system $Ag_2MoO_4 + Na_2MoO_4$ presents a eutectic at 551 °C and $x_{Na2MoO4} = 0.23$. The system $(NaBr)_2 + Na_2MoO_4$ present a eutectic at 526 °C and $x_{Na2MoO4} = 0.70$. The system AgBr + NaBr presents a continuous SL curve showing the existence of solid solutions between the two salts. Analogous

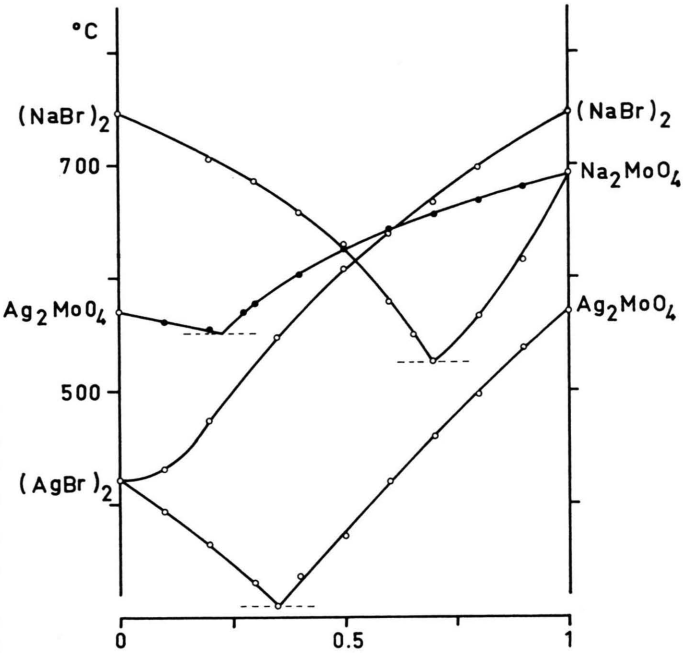

Fig. 2. Binary systems $Ag_2MoO_4 + Na_2MoO_4$, $(NaBr)_2 + Na_2MoO_4$, AgBr + NaBr and $(AgBr)_2 + Ag_2MoO_4$.

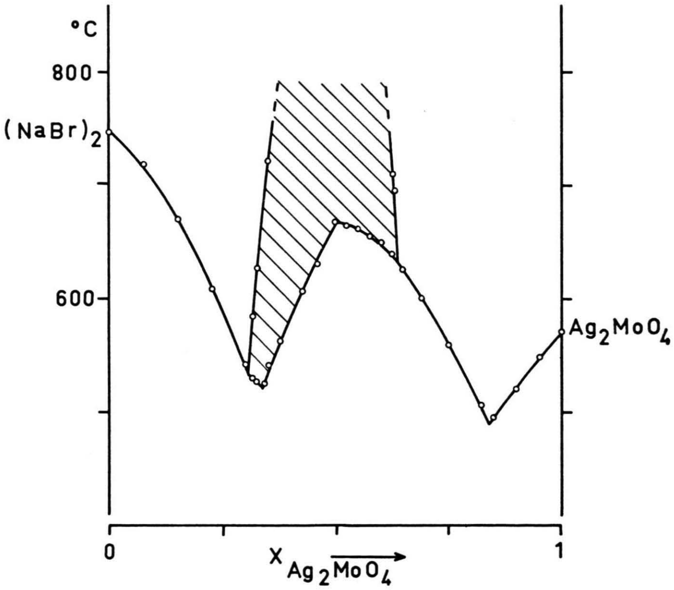

Fig. 3. Unstable diagonal of the reciprocal ternary system $Ag,Na/Br,MoO_4$.

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[10] C. Sinistri and G. Flor, work in press on the "Ric. Sci. (Rome)" and regarding the family of system $Ag,Me/Cl,NO_3$ (Me = Li, Na, K, Rb, Cs).

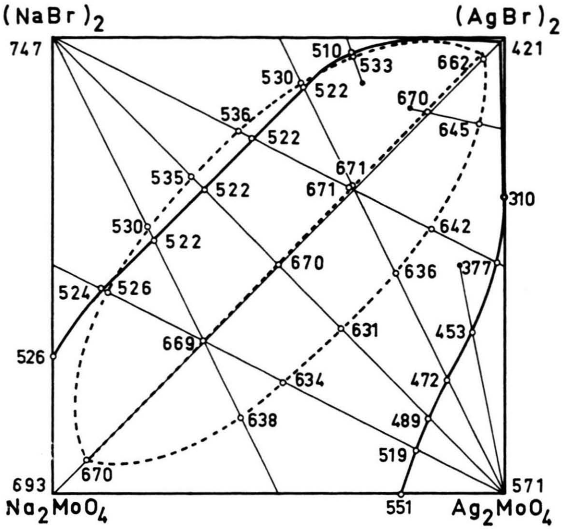

Fig. 4. Diagonal and offdiagonal cuts studied in the reciprocal ternary system Ag,Na/Br,MoO_4 with some significant temperatures.

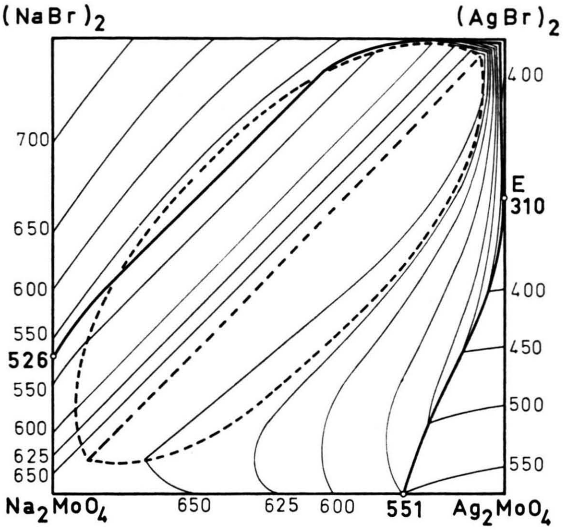

Fig. 5. Projections of the melting diagram of the reciprocal ternary system Ag,Na/Br,MoO_4 with some SL isotherms.

results on this system were reported by Zemczuzny[11]. Finally the system $(AgBr)_2 + Ag_2MoO_4$ presents a eutectic at 310 °C and $x_{Ag2MoO4} = 0.35$.

Fig. 3 reports the SL and LL equilibria in the mixture $(NaBr)_2 + Ag_2MoO_4$, which is the unstable diagonal of the Ag,Na/Br,MoO_4 reciprocal ternary system. The correspondent stable diagonal $(AgBr)_2 + Na_2MoO_4$ appears in Fig. 1.

On the stable diagonal the PCT increases from 662° to 670 °C while $x_{Ag2MoO4}$ increases from 0.04_7 to 0.92_7. On the unstable diagonal the MG extends from $x_{Ag2MoO4} = 0.64$ ($t = 631$ °C) to $x_{Ag2MoO4} = 0.30_5$ ($t = 535$ °C); the maximum of the PCT's is at 670 °C and $x_{Ag2MoO4} = 0.49_5$. For this system Belyaev[1] reports a constant monotectic temperature at 650 °C and a MG extending, at the same temperature, from 93 to 8 AgBr mole %.

Fig. 4 shows the projections of the examined offdiagonal cuts and the temperatures corresponding to significant points of various type. The stratification lens (shaded) impinges on two cristallization fields and occupies the 46.5% of the area of the composition square. The main axis of the lens is slightly rotated in respect to the stable diagonal, as shown by Fig. 4. Along this axis the PCT is 670 ± 1 °C. Finally Fig. 5 reports some SL isotherms and also indicates the position of the ternary eutectic E, which is very close to the binary eutectic in the system $(AgBr)_2 + Ag_2MoO_4$.

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