Short Communications

Topology of the 553 K Isotherm in the Quasi-ternary System Ag,(K,Na)−I,NO₃

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Equilibrium data pertaining to reactions between solid and liquid AgI-based phases and alkali nitrate melts at 553 K have been communicated in a number of papers[1-4] dealing essentially with silver iodide complexation in the nitrate melts. The present interest in AgI-based electrolytes makes it highly desirable to obtain a schematic overview of the phase relationships in systems of this kind. Therefore, we have supplemented the previously published data with liquid-liquid distribution measurements at 553 K in systems $AgI - AgNO_3 - MNO_3$, where M stands for an equimolar mixture of K and Na.

All melts were prepared from $p.a.$ grade chemicals which were pre-treated prior to use as described elsewhere.[2] The melts were equilibrated for 24 h or more under vigorous stirring in Pyrex glass tubes in an aluminium block furnace.[5] AgI-rich and MNO_3-rich melts were separated from each other and analyzed for silver and iodide as described in previous papers.[2,4]

The melt compositions are indicated by cationic mol fractions x_M $(=1-x_{Ag})$ and anionic mol fractions x_I $(=1-x_{NO_3})$. Although all systems have an over-all cation balance $n_K/n_{Na}=1$, this ratio may be significantly different from unity in separate phases ($cf.$ Ref. 4).

The topology of the 553 K isotherm in the quasi-ternary system $Ag,(K,Na)−I,NO_3$ may now be depicted by use of the present and previously published data.[1-4] Fig. 1 gives the phase diagram. There are four single phase areas. The limiting compositions of these four phases, designated by letters a−m, are listed in Table 1. The solids are MI, which stands for solid solution (K,Na)I, and α-AgI-based solid solutions (Ag,M)(I,NO₃) (ss) in
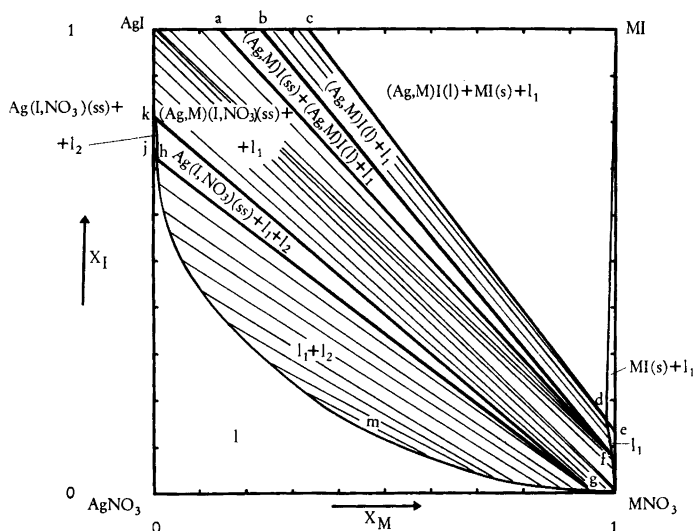

Fig. 1. The 553 K isotherm of the quasi-ternary system $Ag,M − I,NO_3$. M stands for a mixture of K and Na with the over-all ratio $n_K/n_{Na}=1$. Further details are given in the text.

Table 1. The limiting compositions of solid (s) and liquid (l) systems, denoted a−m in the phase diagram.

System	x_M	x_l
a (s)	0.145	1
b (l)	0.233	1
c (l)	0.335	1
d (l)	0.979	0.158
e (l)	1	0.128
f (l)	0.995	0.079
g (l)	0.942	0.001
h (l)	0.005	0.721
j (l)	0	0.74
k (s)	0	0.81
m (l)	0.45	0.14

the range k − AgI − a. This area is best described as a solution of $AgNO_3$ in α-AgI in the range k − AgI, approaching pure AgI in the upper left corner of the diagram, and a solution of KI in α-AgI in the range a − AgI, also approaching pure AgI in the corner. Upper limits for the $AgNO_3$ content in the region AgI − a and the KI content in the region AgI − k can be derived from equilibrium data of Refs. 1 and 4 and Refs. 1 and 3, respectively. In the range AgI − a x_{NO_3} is calculated to $\leq 8 \times 10^{-6}$ and $x_M \leq 2 \times 10^{-7}$ is obtained for the AgI-k region, so the entire k − a area does, in fact, not extend from the axes into the interior of the diagram to any greater extent. Analogously the single phase region b − c is best described as a liquid (Ag,M)I(l), M being essentially K,[2] with $x_{NO_3} \leq 5 \times 10^{-10}$ as calculated from the data of Refs. 3 and 4. The fourth single phase area is the liquid l in the phase diagram. For the sake of clarity, melts having $x_M > 0.45$, corresponding to the critical point m on the binodal curve, are denoted l_1. Analogously those with $x_M < 0.45$ are denoted l_2 in the diagram. In the vicinity of MNO_3 the liquid range extends along the diagonal MNO_3 − AgI to $x_{Ag} = x_l = 2.5 \times 10^{-6}$.[1]

Two-phase regions with selected tie-lines included and invariant three-phase fields are marked in the diagram. The two-phase area j − h − k is simply deduced from the rest of the diagram, and no experimental determinations have been made here.

Finally it should be noted that − except for the ranges of solid solubility − the subsystems AgI − MI and AgI − $AgNO_3$ conform closely to the 553 K isotherms in previously published binaries AgI − KI[6,7] and AgI − $AgNO_3$.[8,9] The only report on solid solubility is found in the early work by Scarpa,[8] although the actual solubility of $AgNO_3$ in α-AgI at 553 K appears to be about three times as large as that stated by him.

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