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Complex Formation between Silver and Iodide Ions in Fused Potassium-Sodium Nitrate. II. Phase Transformation at High Iodide Concentrations

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The transition from a solid to a liquid silver iodide phase in equilibrium with iodide-containing melts of equimolar $(K,Na)NO_3$ at 280°C has been studied. At a total iodide concentration of 0.93 mol kg^{-1} in the nitrate phase a solid solution (K,Ag)I(s) transforms into a liquid solution (K,Ag)I(l), in which the mol ratio I:Ag increases from 1.30 to 1.50 when the iodide concentration in the nitrate melt increases from 0.93 to 1.58 mol kg^{-1}. These findings are considered in relation to the phase diagram of the system AgI – KI and the structure of α-AgI.

The solubility of equimolar (K,Na)I(s) in the nitrate melt has been determined at various amounts of $AgNO_3$ added to this melt. The results indicate the presence of AgI_4^{3-} as well as polynuclear species.

In a previous paper[1] potentiometric data on the complex formation between silver and iodide ions in fused equimolar $(K,Na)NO_3$ at 280°C have been reported. The stabilities of the complex ions AgI_2^-, AgI_3^{2-}, and $Ag_2I_6^{4-}$ were determined. Evidence was also found for the presence of AgI_4^{3-}, but the value of the corresponding stability constant could be given only as a rough estimate. Thus, the nature of the complex species richest in iodide is still somewhat unclear. The need for additional studies employing other experimental methods, such as solubility measurements, is obvious. The conventional solubility method, however, cannot be applied to this system at high iodide concentrations. In their study of silver iodide complexes in equimolar melts of KNO_3 and $NaNO_3$ at 280°C, Elding and Leden[2] did not perform solubility measurements at iodide concentrations above 0.8 mol kg^{-1} [*i.e.* mol per kg solvent, $(K,Na)NO_3$]. They found, that a further increase in the iodide concentration made the solid AgI transform into a deeply coloured melt with a density considerably higher than that of the nitrate melt with which it is in equilibrium. Miscibility gaps of this kind have been reported

for similar systems before. Such systems are Na,Ag/NO_3,I[3] and K,Ag/NO_3,I.[4] Different factors that seem to be of importance in determining the extent of immiscibility in this kind of fused salt systems have been thoroughly discussed by Ricci,[5] Marcus,[6,7] and Belyaev.[8] Generally the different character of the chemical bonding in the components of the system contributes to the tendency of liquid immiscibility. Differences in the anion or cation radii and in ion polarizabilities between the constituent ions in the two phases also seem to be of importance for the phase separation. Hence the two liquid phases are expected to exhibit rather different properties.

The present investigation has been undertaken in order to (a) elucidate the phase transition that made an unambiguous interpretation of Elding's and Leden's solubility data difficult; (b) provide additional qualitative information on the complex formation at high ligand concentrations. Such information may be gained from a careful study of the solubility of the ligand (*i.e.* (K,Na)I(s)) in the nitrate melt when various amounts of $AgNO_3$ are added to this melt.

EXPERIMENTAL

Chemicals used. Potassium nitrate and sodium nitrate (Merck, *p.a.*) were powdered, ground together and dried at 120°C for at least ten days. Potassium iodide (Merck, *p.a.*) and sodium iodide (Mallinckrodt, *p.a.*) were dried at 140°C. These chemicals were used without further purification.

Silver iodide was prepared by precipitation from hot dilute solutions of potassium iodide and silver nitrate (Engelhard, *p.a.*). The precipitate was washed with 1 % nitric acid and large amounts of water. After drying for one day at 110°C the silver iodide was stored protected from light.

Apparatus. Large Pyrex test tubes were used as reaction vessels in a high-temperature thermostat bath similar to the one used by Cigén and Mannerstrand.[9] The temperature was maintained at (280 ± 1)°C.

Procedure. For the phase transition investigation, weighed amounts of (K,Na)I (equimolar mixture) and AgI were added to 50.00 g of liquid (K,Na)NO_3 (equimolar mixture), and the system was agitated by vigorous stirring with a Pyrex propeller. Equilibrium was attained within less than 40 h. After equilibration the system was allowed to stand without stirring for at least 1 h in order to effect properly separated phases.

Samples from the nitrate phase were taken with a pre-heated pipette. Samples from the heavy, liquid AgI phase were isolated from the system in the following way.

One end of a Pyrex glass tube (inner diameter 5 mm) was drawn to a fine capillary, which was introduced into the liquid AgI phase, while the other end of the tube was closed. Then the liquid was sucked up into the tube through the capillary. The sample was poured out into a small beaker, thermostated at 280°C, where the procedure could be repeated. It appeared that one separation of this kind is enough to eliminate all observable traces of the nitrate phase. The distribution of Ag and I between the two phases was determined in systems containing 4.50 g AgI. The total concentrations of silver and iodide in the nitrate melt were determined. Samples from the liquid AgI phase were isolated and analyzed for silver and iodide and in some cases for sodium and potassium. Occasional qualitative tests for nitrate were also made.

The solubility of (K,Na)I was measured in systems containing 50.00 g (K,Na)NO_3, 21.00 g (K,Na)I and various amounts of $AgNO_3$.

Some melts with high iodide concentrations were analyzed for iodide after 10 days at 280°C. No oxidation of iodide could be detected.

Analyses. The silver content was determined by electroanalytical precipitation on a rotating platinum cathode from hot cyanide solutions.

For the iodide analyses the solidified samples were suspended in an aqueous dex-

trin solution (in order to prevent coagulation of AgI). The amount of iodide not present as solid AgI was determined by titration with a standard $AgNO_3$ solution using eosine as indicator. The total amount of iodide was calculated from these titration data and the known value of the silver content. The iodide analyses were reproduced to ± 0.5 % or better.

The content of alkali metal ions was determined from atomic absorption measurements on samples dissolved in 50 mM cyanide solutions.

X-Ray powder photographs of samples from the liquid AgI phase were recorded in a Hägg-Guinier camera within a few hours after the sample had been quenched. Another powder photograph of each specimen was recorded after three days. No change in the diffraction pattern could be detected.

RESULTS AND DISCUSSION

The following symbols are used:

n_A = amount of species A.
y = mol ratio n_I/n_{Ag} in the iodide phase.
q_{Na} = $n_{Na}/(n_{Na}+n_K+n_{Ag})$, calculated for the iodide phase.
x_K = $n_K/(n_K+n_{Na})$, calculated for the system as a whole.
C_{Ag} = total concentration of silver(I) in the nitrate melt.
C_I = total concentration of iodide in the nitrate melt.
$\bar{n}$ = $(C_I-[I^-])/C_{Ag}$, the average ligand number.

The phase transition. The only components of importance in the liquid AgI phase are AgI and KI. No nitrate could be detected, and from the figures of Table 1 it follows that sodium accounts for less than 0.3 % of the total cation amount. Therefore, the sodium content has been ignored in the calculation of the composition of the AgI phase. The traces of sodium might possibly result from contamination by the nitrate melt, but this view is to some degree contradicted by the monotonous variation in q_{Na} with y.

Table 1. The sodium ratio q_{Na} at different values of y in the liquid AgI phase.

y, $q_{Na} \times 10^3$;									
1.304,	1.0;	1.360,	1.4;	1.423,	2.1;	1.469,	2.7;	1.503,	2.8

The composition of the liquid AgI phase has been directly determined from the silver and iodide analyses. For the solid phase, which is difficult to separate quantitatively from the nitrate melt, the composition is calculated from the difference between the added and found amounts of iodide in the nitrate melt. Fig. 1 shows y as a function of C_I.

The phase transition occurs at $C_I = (0.930 \pm 0.006)$ mol kg^{-1} (*vide* Table 2). The point in Fig. 1 marked with a half-filled circle refers to a three-phase system where the liquid nitrate and AgI phases are in equilibrium with solid (K,Na)I. Hence, the range of existence for the liquid AgI phase at 280°C is $1.30 \leq y \leq 1.50$. For the solid AgI phase y deviates markedly from 1 in

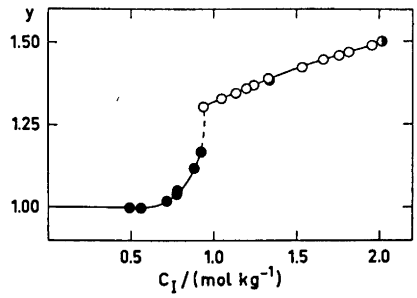

Fig. 1. Variation of y with C_I. Symbols: (K,Ag)I(s) (●), (K,Ag)I(l) (○), three-phase system (K,Ag)I(l) – (K,Na)I(s) – nitrate melt (◑).

Table 2. The equilibrium compositions of the nitrate and iodide phases. Data of the left hand side of the table refer to systems (K,Ag)I(s)-nitrate melt; those of the right hand side refer to (K,Ag)I(l)-nitrate melt.

C_I / mol kg^{-1}	C_{Ag} / mol kg^{-1}	y	C_I / mol kg^{-1}	C_{Ag} / mol kg^{-1}	y
0.492	0.00789	1.00	0.936	0.0300	1.304
0.561	0.00937	1.00	1.048	0.0374	1.330
0.715	0.01672	1.02	1.132	0.0456	1.347
0.773	0.01994	1.04	1.198	0.0479	1.360
0.779	0.02065	1.05	1.241	0.0528	1.370
0.881	0.02690	1.12	1.329	0.0603	1.389
0.923	0.02969	1.17	1.333	0.0596	1.386
			1.533	0.0810	1.423
			1.661	0.0927	1.446
			1.755	0.1039	1.459
			1.817	0.1110	1.469
			1.954	0.1293	1.489
			2.013	0.1330	1.503[a]

[a] In equilibrium with solid (K,Na)I.

a narrow concentration range preceding the solid-liquid transition. This obviously means that KI migrates into the high-temperature modification of silver iodide, α-AgI, forming a solid solution. At $C_I = 0.93$ mol kg^{-1} the concentration of potassium iodide in the solid phase is high enough to make the iodide lattice of the α-AgI collapse – the solid melts. (From the measurements reported here it is of course impossible to distinguish between KI and NaI in the *solid* solution. The reluctance of AgI to accept NaI in liquid solution at this temperature suggests, however, that KI is the solute in the solid as well.)

Extensive investigations of systems of the type AgI – MI have been made recently by Burley and Kissinger [10] and by Bradley and Greene.[11,12] Burley and Kissinger claim that the AgI – KI system contains one compound, KAg_3I_4, stable up to 268°C, where it melts congruently. No solid solution was indicated.

According to Bradley and Greene,[11] the AgI – KI system contains two intermediate compounds, K_2AgI_3 and KAg_4I_5. K_2AgI_3 disproportionates to solid KAg_4I_5 and KI at 130°C. The compound KAg_4I_5 is stable between 38°C and 253°C. Below 38°C it disproportionates to the hexagonal β-AgI and K_2AgI_3. At 253°C KAg_4I_5 melts incongruently. No solid solutions have been reported. Topol and Owens [13] later verified the diagram published by Bradley and Greene in all essentials.

Thus, AgI and KI do not form any solid intermediate compound at 280°C. According to Bradley and Greene, the system is liquid in a range between 23 and 34 mol % KI at this temperature. The limits $1.30 \leq y \leq 1.50$ for the liquid AgI phase in the systems studied in this work are in perfect agreement with these figures.

The consistency with the findings of Bradley and Greene has been further confirmed by X-ray diffraction measurements on powder of quenched samples of the liquid AgI phase. All samples gave identical powder photographs where no traces of KI could be detected. The diffraction pattern showed that the samples consisted of β-AgI and K_2AgI_3. The structure of the latter compound has been determined by Brink and Kroese.[14] For comparison powder photographs from a model powder were recorded. This powder was made by melting together KI and AgI in the mole proportions 1:3 at 280°C followed by a rapid cooling to room temperature. The model powder and the samples from the liquid AgI phase gave identical diffraction patterns.

Thus, there is good agreement with the phase diagram of Bradley and Greene except for the rather narrow range where a solid solution of KI in α-AgI has been observed in this work.

In the solid α-AgI, which is stable above 146°C, the iodide ions are arranged in a body-centered cubic lattice [15,16] while the silver ions are thought to be randomly distributed over a large number of sites. A formation of solid solution with, for instance, those alkali metal iodides where no sterical obstacles arise, should obviously be facilitated by this type of structure. This fact has also been stressed by Krogh-Moe [17] in his discussion of different factors of importance for formation of solid solutions with compounds of B 23 structure.

The crystal ionic radii of K^+ and Ag^+ are not very different: 1.33 Å and 1.26 Å, respectively. The potassium ions might possibly be accommodated in the 12d positions, which are the largest cation sites in α-AgI. Such an arrangement can not be realized, however, without a considerable distortion of the iodide lattice. This might be the cause of the final breakdown of the crystal structure at a critical concentration of potassium ion, which is reached at the point of phase transition.

The ligand solubility. The solubility of (K,Na)I(s) at various C_{Ag} has been determined for $0 \leq C_{Ag} \leq 0.13$ mol kg^{-1} and the results are given in Table 3.

It is well known that KI and NaI form a continuous range of solid solutions at high temperatures.[18–20] No solid solution or intermediate compound with KNO_3 or $NaNO_3$ is found at 280°C.[20] Furthermore, it appeared from the analyses for silver in the nitrate melt that no detectable amounts of $AgNO_3$ are present in the solid (K,Na)I at equilibrium. Separate experiments have shown that the solubility of (K,Na)I in fused (K,Na)NO_3 is independent of

Table 3. The solubility of (K,Na)I at different C_{Ag} and the corresponding ligand numbers, $\bar{n}_{exp}$. For comparison the ligand numbers, calculated from the set of stability constants of Ref. 1 ($\bar{n}_{calc}$) are included.

C_{Ag} / mol kg^{-1}	C_I / mol kg^{-1}	$\bar{n}_{exp}$	$\bar{n}_{calc}$
0	1.577		
0.01121	1.611	3 ± 1	3.07
0.02470	1.659	3.3 ± 0.4	3.06
0.03984	1.707	3.3 ± 0.2	3.05
0.04919	1.735	3.2 ± 0.1	3.05
0.0619	1.773	3.19 ± 0.08	3.04
0.0761	1.816	3.14 ± 0.08	3.04
0.0913	1.858	3.08 ± 0.07	3.04
0.0955	1.868	3.05 ± 0.06	3.04
0.1087	1.906	3.02 ± 0.05	3.03
0.1199	1.936	3.00 ± 0.05	3.03
0.1300	1.965	2.98 ± 0.04	3.03

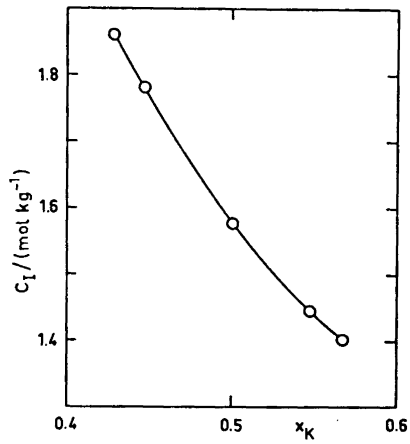

Fig. 2. The solubility of (K,Na)I(s) at various x_K. $C_{Ag} = 0$.

the mass ratio of solid (K,Na)I to liquid (K,Na)NO_3, indicating that the ratio n_K:n_{Na} is the same (*i.e.* 1:1) in the solid and in the nitrate melt. On the other hand, there is a strong dependence on the K − Na balance in the entire system. This is illustrated in Fig. 2 where the solubility, C_I, is given for $C_{Ag} = 0$ as a function of x_K around $x_K = 0.5$.

At $x_K = 0.500$ the solubility in pure (K,Na)NO_3 is 1.577 ± 0.004 mol kg^{-1}. In systems containing silver(I) there is an appreciable increase of the solubility for increasing C_{Ag}. Since x_K has been kept constant at 0.500 in all systems investigated, it is very reasonable to assume the free iodide concentration, [I$^-$], to be 1.58 mol kg^{-1} in melts containing silver(I) as well. Hence, the mean ligand number $\bar{n}$ may be directly calculated from the corresponding values of C_{Ag} and C_I. In Table 3 the ligand numbers evaluated

in this direct way are compared with values calculated from the set of stability constants given in Ref. 1.

Two important pieces of information about the higher complexes can be derived from the experimental $\bar{n}$-data: (a) The monotonous variation of $\bar{n}$ with C_{Ag} at $[I^-] = 1.58$ mol kg^{-1} indicates that polynuclear species are present since $\bar{n}$ is a function solely of the free ligand concentration in a mononuclear complex system;[21] (b) Despite the poor accuracy in the $\bar{n}$-values at the smallest C_{Ag} (due to small differences $C_I - [I^-]$), it is evident that $\bar{n}$ exceeds 3 at low C_{Ag}, indicating the presence of AgI_4^{3-}.

The $\bar{n}_{exp}$-values of Table 3 show a more pronounced decrease with increasing C_{Ag} than do the $\bar{n}_{calc}$-values. At high C_{Ag} the two sets of $\bar{n}$-values coincide. The reason for this trend might be a too low value of the stability constant β_{41} of AgI_4^{3-} calculated from the emf measurements in unsaturated melts. This possibility has been discussed in a previous paper.[1]

A more thorough discussion of the complex formation at high C_I will appear in a subsequent paper,[22] treating the distribution equilibria between (K,Ag)I(s) or (K,Ag)I(l) and the nitrate melt.

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REFERENCES

1. Holmberg, B. *Acta Chem. Scand.* **27** (1973) 875.
2. Elding, I. and Leden, I. *Acta Chem. Scand.* **23** (1969) 2430.
3. Zakharchenko, M. A. and Bergman, A. G. *J. Gen. Chem. USSR* **25** (1955) 833.
4. Dombrovskaya, N. S. and Koloskova, Z. A. *Izv. Sektora Fiz. Khim. Anal., Inst. Akad. Nauk SSSR* **22** (1953) 178.
5. Ricci, J. E. In Blander, M., Ed., *Molten Salt Chemistry*, Interscience, New York 1964, p. 239.
6. Marcus, Y. In Dyrssen, D., Liljenzin, J. O. and Rydberg, J., Eds., *Solvent Extraction Chemistry*, North-Holland, Amsterdam 1967, p. 555.
7. Marcus, Y. In Braunstein, J., Mamantov, G. and Smith, G. P., Eds., *Advances in Molten Salt Chemistry*, Plenum Press, New York 1971, Vol 1, p. 76.
8. Belyaev, N. *Russian Chem. Rev.* **29** (1960) 428.
9. Cigén, R. and Mannerstrand, N. *Acta Chem. Scand.* **18** (1964) 1755.
10. Burley, G. and Kissinger, H. E. *J. Res. Natl. Bur. Std.* **A 64** (1960) 403.
11. Bradley, J. N. and Greene, P. D. *Trans Faraday Soc.* **62** (1966) 2069.
12. Bradley, J. N. and Greene, P. D. *Trans. Faraday Soc.* **63** (1967) 424.
13. Topol, L. E. and Owens, B. B. *J. Phys. Chem.* **72** (1968) 2106.
14. Brink, C. and Kroese, H. A. S. *Acta Cryst.* **5** (1952) 433.
15. Strock, L. W. *Z. physik. Chem. Leipzig* **25** (1934) 441.
16. Hoshino, S. *J. Phys. Soc. Japan* **12** (1957) 315.
17. Krogh-Moe, J. In Førland, T., Grjotheim, K., Motzfeldt, K. and Urnes, S., Eds., *Selected Topics in High Temperature Chemistry*, Univ. førl., Oslo 1966, p. 79.
18. Kurnakow, N. S. and Zemczużny, S. F. *Z. anorg. Chem.* **52** (1907) 186.
19. Bergman, A. G. and Platonov, F. P. *Izv. Sektora Fiz. Khim. Anal., Inst. Akad. Nauk SSSR* **10** (1937) 253.
20. Vasenin, F. I. and Bergman, A. G. *Izv. Sektora Fiz. Khim. Anal., Inst. Akad. Nauk SSSR* **11** (1938) 169.
21. *E.g.* Rossotti, F. J. C. and Rossotti, H. *The Determination of Stability Constants*, McGraw, New York 1961.
22. Holmberg, B. *Acta Chem. Scand.* **27** (1973) 3657.

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