The Structure of Ag_4Br^{3+} in Molten Alkali-Metal Nitrate

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Molten mixtures of $AgNO_3$–(K,Na)NO_3 and AgBr–$AgNO_3$–(K,Na)NO_3 have been investigated by liquid X-ray scattering and Raman spectroscopic techniques at 280 °C. The coordination of silver(I) by nitrate ions was shown to be asymmetric and bidentate, with the metal ion out of the nitrate plane. The two shortest Ag–O distances are 2.43 and 3.16 Å (cf. 2.45 and 3.05 Å in Ref. 1). The coordination geometry is less open than that observed in melts more concentrated in Ag(I). The structure of the complex Ag_4Br^{3+} was investigated. Four Ag–Br distances can be identified at 2.62 Å, indicating that the bonds are of significant covalency. However, no distinct Ag–Ag separations can be detected. A large freedom of movement of Ag^+ is a likely explanation for these results, which are in good agreement with literature data on similar AgX–Ag_2O–AgOx (X = Cl, Br, I; Ox = oxoanion) ion-conducting glass systems.

Silver(I) and halide ions are known to form polysilver complexes Ag_mX^{m-1} (X = Cl, Br, I; m = 2–4) in solid phases and various liquid solutions. This kind of polysilver chemistry has been reviewed fairly recently by Holmberg.[1-4] The ions Ag_4X^{3+} (X = Br, I) were identified in the molten (K,Na)NO_3 solvent.[2,3] The structural characteristics of Ag_4I^{3+}, as determined by liquid X-ray scattering in both (K,Na)NO_3 and aqueous solution, are puzzling.[1,4] Four distinct Ag–I distances at 2.8 Å have been identified. These distances are of the same magnitude as those in solid AgI and the corresponding AgI_4^{3-} complex and they indicate a significant orbital overlap between the silver and iodide atoms. However, no Ag–Ag correlation in Ag_4I^{3+} could be detected either in the melts or in nitrate- or perchlorate-based aqueous solutions. One way of describing the local structure around the iodide ion would be to consider the silver ions as floating on an electron surface of the large iodide ion.

Ag^+ has a d^{10} valence ground-state electron configuration. Other d^{10} ligand cation systems with central halide ions have completely different properties. Mercury(II) forms the very electroactive species Hg_2Cl^{3+} in dimethyl sulfoxide (DMSO) solution.[5] Although Hg_2Cl^{3+} constitutes only a minor fraction of the mercury present in the solution, this type of complex is responsible for the major part of electron transfer to an electrode surface. The structure of the corresponding iodide complex Hg_2I^{3+} is, in contrast to that of Ag_4I^{3+}, well-defined. The Hg–I–Hg angle is 90° in both DMSO and aqueous solution.[6] Remarkably enough, cadmium(II) does not seem to form any polycadmium species in any solvent investigated to the present date.[7] The basic reasons for the disparate properties of these superficially similar d^{10} systems are at present not known. In particular, no model explains in a satisfying way the puzzling structural characteristics of Ag_4I^{3+}.

It is thus of great interest to investigate whether the unusual structural properties of Ag_4I^{3+} are unique, or may be significant for Ag_4Br^{3+} as well. The nitrate coordination to uncomplexed silver(I) and the structure of Ag_4Br^{3+} have thus been characterized in molten AgBr–$AgNO_3$–(K,Na)NO_3 systems of appropriate compositions, by use of liquid X-ray scattering and Raman spectroscopic methods.

Experimental

Chemicals. KNO_3 and $NaNO_3$ (Riedel-de Haën, p. A.) were dried at 130 °C, while $AgNO_3$ (Merck, p. A.), AgBr (Merck, 99 %) and AgI (Ventron, 99.9 %) were dehydrated over anhydrous $Mg(ClO_4)_2$ for several days before use.

Liquid X-ray scattering and Raman spectroscopy. The composition and physical properties of the melts investigated by liquid X-ray scattering are given in Table 1. Raman spectra of these melts and two AgI–$AgNO_3$–(K,Na)NO_3 melts with C_I = 0.3 and 1.0 mol kg^{-1} and C_{Ag} = 4.0 and 10.0 mol kg^{-1} respectively, were also recorded and analyzed. The instrumentation and experimental procedures have been thoroughly described previously.[8-11]

Results and discussion

Nitrate coordination to silver(I). A structure analysis of the pure solvent (K,Na)NO_3 has been given previously.[8] The results of the present liquid X-ray scattering study on $AgNO_3$–(K,Na)NO_3 melts are displayed in Fig. 1 and Table 2. The results indicate a coordination mode with four nitrates on the average attached to the silver ions in a flat-on

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Table 1. The composition, stoichiometric unit volume per silver atom, mass density and linear absorption coefficient of the melts investigated by liquid X-ray scattering.

System	C_K[a]	C_{Na}[a]	C_{Ag}[a]	C_{NO_3}[a]	C_X[a]	V/Å^3	ϱ/g cm^{-3}	μ/cm^{-1}
$AgNO_3$–(K,Na)NO_3	7.77	7.77	5.78	21.32	–	287.2	2.43	23
AgBr–$AgNO_3$–(K,Na)NO_3	7.68	7.68	5.71	20.62	0.44	290.9	2.41	26

[a]All concentrations given in mol dm^{-3}.

bidentate manner, which is analogous to that previously found for the ions Pb^{2+}, Cd^{2+} and Tl^+.[7,8,12] The configuration is less open than that proposed by Holmberg and Johansson.[1] The NO_3^-/Ag^+ ratio in the melts examined in Ref. 1 was, however, considerably lower than four. This fact suggests that the nitrate ions in systems more concentrated in Ag(I) have to be shared between silver ions to a larger extent, with a more open average coordination mode as a consequence.

The shortest Ag–O distances of 2.43 and 3.16 Å (cf. 2.45 and 3.05 Å in Ref. 1) seem to be rather unaffected by composition changes. The Raman spectra of molten $AgNO_3$–(K,Na)NO_3 mixtures display a broad band on the Rayleigh shoulder at ca. 100–200 cm^{-1}, but no distinct Ag–O vibration modes can be detected. These results are in good agreement with the observations in $Pb(NO_3)_2$–(K,Na)NO_3 melts.[8]

Polysilver complexes. The partial exchange of NO_3^- for Br^- in the $AgNO_3$–(K,Na)NO_3 melts causes a significant peak at about 2.6 Å in the differential reduced radial distribution function (differential rRDF), as seen in Fig. 2. The introduction of bromide to a (K,Na) NO_3 melt gives rise to Na–Br and K–Br peaks at 2.78 and 3.31 Å, but such contributions are significant only at concentrations higher than those used here.[19] The 2.6 Å peak is thus attributed to Ag–Br interactions. Analogously to the corresponding iodide systems, no other significant structural changes can be traced.[1,4] However, the new peak is fairly broad, with a shoulder on the long-distance side. A least-squares analysis of the 2.6 Å peak, using the model for $AgNO_3$–(K,Na)NO_3 as a refinement basis, gives only 1–2 Ag–Br distances per bromide and an unrealistically large value of the *b*-parameter. The 3 Å shoulder, in combination with the low frequency of Ag–Br distances obtained, indicate that effects from Ag^+–NO_3^- release upon complexation with bromide are significant. More pronounced effects of this type have previously been observed in PbX_2–$Pb(NO_3)_2$–(K,Na)NO_3 melts (X = F, Cl, Br, OH),[8,13] for which the structural parameters for the Pb–X contributions not could be evaluated by a straightforward least-squares procedure. The nitrate release is observed in the Raman spectra as a reduction in intensity of the broad band at about 100–200 cm^{-1} for the most concentrated AgI–$AgNO_3$–(K,Na)NO_3 melt. This is the only observable effect of the introduction of halides to the $AgNO_3$–(K,Na)NO_3 melts, since no Ag–X bands could be detected. For these reasons the number of Ag–O_I and Ag–O_{II} distances per silver(I) was allowed to vary in the least-squares refinements of the structural parameters in an Ag_4Br^{3+} complex. The number of Ag–Br

Table 2. Parameters used for calculation of the theoretical curves in Fig. 1; *d* = interatomic distance, *b* = temperature coefficient and *n* = number of interactions.[a]

Interaction	(K,Na)NO_3[b]			$AgNO_3$–(K,Na)NO_3		
	d/Å	*b*/Å^2	*n*	*d*/Å	*b*/Å^2	*n*
Ag–O_I				2.43(1)	0.012(1)	4.1(1)[d]
Ag–O_{II}				3.16(1)	0.011(1)	4.1(1)[d]
Ag–O_{III}				3.66(2)	0.038(3)	4.3(2)[d]
Ag–N				2.83(1)	0.010(1)	4.2(2)[d]
K–O	3.13(2)	0.035(3)	2.9(2)[c]			
Na–O	2.71(1)	0.017(2)	3.4(2)[c]			
K–K	4.75(2)	0.020(2)	0.55(3)[c]			0.37(5)[c]
K–Na	4.29(1)	0.041(2)	2.06(7)[c]			0.99(9)[c]
Na–Na	4.06(4)	0.038(9)	0.6(1)[c]			0.51(16)[c]
O–O	5.23(2)	0.051(4)	7.9(4)[c]			4.4(7)[c]
Ag–Ag				4.24(4)	0.037(6)	0.051(7)[c]
Ag–K				4.34(2)	0.040(3)	0.41(3)[c]
Ag–Na				3.90(3)	0.047(7)	0.46(4)[c]

[a]The data given for (K,Na)NO_3(l) served as a basis in the refinements of the parameters of the $AgNO_3$–(K,Na)NO_3 melt. Refined parameters are given with one mean error in brackets. [b]From Ref. 15. [c]Per nitrate. [d]Per silver(I) atom.

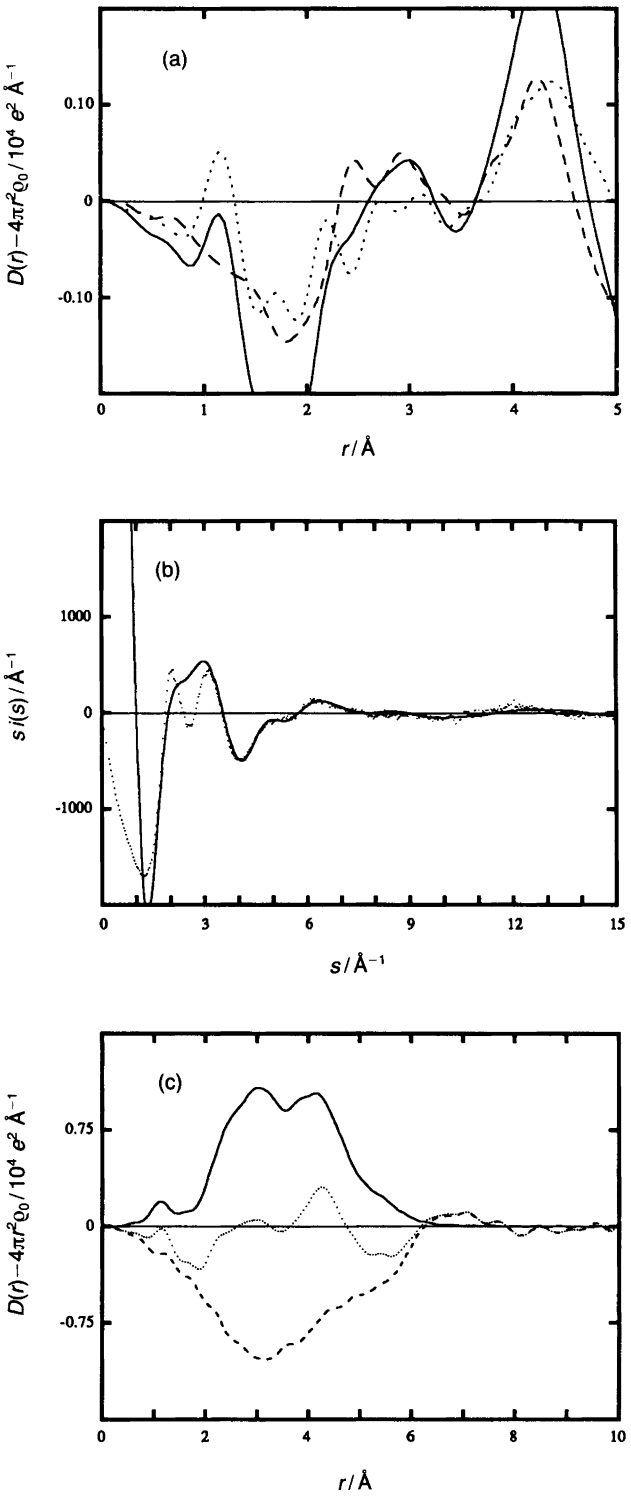

Fig. 1. The experimental results and the theoretical model for the $AgNO_3$–(K,Na)NO_3 melt: (a) the differential rRDF (- - -) between the $AgNO_3$–(K,Na)NO_3 (——) and (K,Na)NO_3 (····) melts; (b) the reduced intensity function of the theoretical model and experimental points; (c) the experimental reduced RDF (——) and the theoretical peak shapes according to the atomic parameters in Table 2 (····), and their difference (- - -).

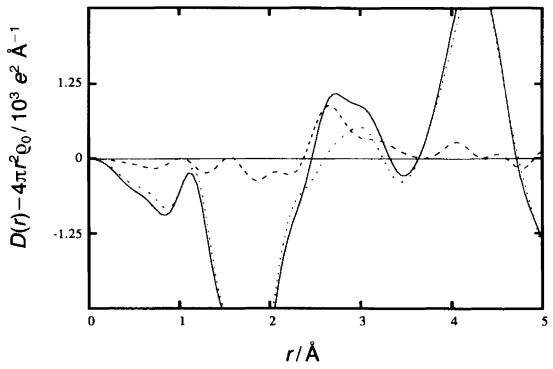

Fig. 2. The differential reduced radial distribution function (- - -) between the AgBr–$AgNO_3$–(K,Na)NO_3 (——) and $AgNO_3$–(K,Na)NO_3 (····) melts.

distances obtained by such an approach is 3.9. All the parameters of the refinement are shown in Table 3.

The Ag–Br distance of 2.62 Å is only slightly shorter than 2.68 Å, which is observed in solid $AgI_{1-x}Br_x$ solutions with a characteristic coordination number of four.[14] The Ag–Br distance in pure AgBr(s) and $AgBr_{1-x}I_x$ solid solutions with a rock-salt structure and a characteristic coordination number of six is about 2.88 Å.[15]

The applied structural model, involving only four Ag–Br interactions per bromide and no Ag–Ag correlations in the Ag_4Br^{3+} complex in the melt investigated, also gains support from several pieces of independent circumstancial evidence, summarized below.

(1) The thermodynamic results of the silver(I) iodide and bromide systems in molten (K,Na)NO_3 are very similar. Both solubility and potentiometric experiments identify Ag_4X^{3+} as the predominating polysilver species for the melt compositions investigated.[2,3]

(2) No difference in Raman spectroscopic results was observed for the AgX–$AgNO_3$–(K,Na)NO_3 melts (X = Br, I) in this study, i.e. Ag–X vibration modes were not detected in either system. There is thus no Raman spectroscopic evidence that Ag_4Br^{3+} should be of a fundamentally different nature than Ag_4I^{3+}. The halide concentrations of the melts investigated were low compared to analogous

Table 3. Refined atomic parameters for the AgBr–$AgNO_3$–(K,Na)NO_3 melt; d = interatomic distance, b = temperature coefficient and n = number of distances.[a]

Interaction	d/Å	b/Å^2	n
Ag–Br	2.62(1)	0.014(3)	3.9(3)[b]
Ag–O_I			3.2(2)[c]
Ag–O_{II}			5.1(2)[c]

[a]The results obtained for the $AgNO_3$–(K,Na)NO_3 melt served as refinement basis. The parameters are given with one mean error in brackets. [b]Per bromide. [c]Per silver(I).

glass systems for which Ag–X vibration modes have been detected.

(3) The differential rRDFs of the silver bromide and iodide systems display the same basic type of structural pattern, as mentioned previously. If Ag_4Br^{3+} has a tetrahedral configuration, the differential rRDF would have displayed a significant Ag–Ag peak at about 4.3 Å. No trace of such a peak is observable (Fig. 2).

(4) There exist a vast number of Ag^+ ion-conducting AgX-doped glasses (X = Cl, Br, I), with both discrete and and network-forming oxoanions. Such systems are electrostatically very similar to the $AgX–AgNO_3–(K,Na)NO_3$ melts studied in this work. The results obtained by different structural investigations are summarized as follows: (a) *Low-frequency Raman spectroscopy:* Ag–X vibration modes at 190, 135 and 115 cm^{-1} for X = Cl, Br and I respectively, have been reported. The broad lineshapes of these bands have been interpreted in terms of amorphous tetrahedral AgX clustering. The intensity of the signals is low and decreases from iodide to chloride.[16–21] (b) *EXAFS and XANES:* The addition of AgX only seems to affect the host glass structure marginally. The silver halides are thus most likely confined to interstices in the glass. The Ag–Br distances observed in the radial distribution functions are normally 2.62–2.64 Å (cf. Ref. 14 and the present study). Least-squares analyses using solid AgBr with a rock-salt structure as a model substance, however, give Ag–Br distances of 2.76–2.77 Å. Those values are apparently not independent of the choice of model substance.[22–30] (c) *X-ray and neutron scattering:* The host glass structure seems to be essentially unaffected by additions of AgX. The silver halides are most likely accomodated in cavities and voids in the host glass. A typical Ag–Br distance is 2.64–2.66 Å, which is in good agreement with the present results.[31–34] The microstructure is well described by a fractal formalism. Ag–Ag and/or I–I correlations are observed, but it is concluded that any type of microclusters present must be smaller than about 10 Å. The formation of amorphous clusters with a typical size of 8 Å in voids or interstices of the host glass structure is proposed in the most recent papers.[35–43] Since the silver/halide ratio is larger than or about one in these glasses, reasonable candidates are polysilver Ag_4X^{3+} aggregates, which typically have a diameter of *ca.* 8 Å.

The present structural investigation thus confirms that Ag_4Br^{3+} is the predominating species in the $AgBr–AgNO_3–(K,Na)NO_3$ melts. Furthermore, the bromide complex, by analogy with Ag_4I^{3+}, has a large freedom of Ag^+ movement on the surface of the central anion. It is also suggested that the local Ag(I) structure and dynamics around Br and I in the nitrate melts are basically of the same nature as that of ion-conducting AgX–oxoanion glasses.

The nature of the chemical bonding in systems of this type is still obscure. In this context it is worth noting that α-AgI(s), AgX-based solid solutions (X = Cl, Br, I), as well as the silver(I) halide doped glasses, are also excellent Ag^+ ion conductors, a property not observed for the corresponding d^{10} cadmium(II) and mercury(II) systems.[14–16,35,44] Furthermore, the coinage metals form a vast number of solid compounds with extemely short metal–metal separations and unusual coordination geometries, attributed to homoatomic $d^{10}–d^{10}$ interactions.[45] Valence orbital mixing has been suggested as important in such systems.[46] Ag_2^{2+} pairs, supported by chloride bridges, are formed in a NaCl matrix,[47,48] and theoretical calculations suggest that Ag_m^{y+} clusters ($y < m$) are stabilized by the addition of electrons into hybrid orbitals of the *s–d* type.[49,50] Studies of the magnetic susceptibility and electron density distribution in solid silver halides show that the physical properties of these solid compounds are well-described by assuming a careful balance between simple ionic and covalent valency $Ag(4d–5s)–X(np)$ interactions.[50] All these bonding theories are in good agreement with the thermodynamic and structural properties observed for polymetal complexes of heavy main-group metal ligands in general, summarized in Ref. 9.

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