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Coordination of Silver(I) by Thiocyanate, Cyanide, and Iodide in Molten KSCN, KSCN–KCN, and KSCN–KI Mixtures at 185 °C. An X-ray Scattering and Emf Study

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The coordination of silver(I) by thiocyanate in (K,Ag)SCN melts has been investigated by X-ray scattering. It is concluded that silver is surrounded by four thiocyanate ions, coordinating through the sulfur end at a distance of 2.57 Å, which agrees with the observed distance for tetrahedrally coordinated Ag(I) in the solid state. The stepwise formation of mononuclear iodide and cyanide complexes with silver in molten KSCN has been investigated at 185 °C. Measurements were performed as potentiometric titrations, recording changes in the silver activity, in systems (K^+, Ag^+)–(SCN^-, I^-) and (K^+, Ag^+)–(SCN^-, CN^-). Stability constants for two consecutively formed complexes in the iodide system and three complexes in the cyanide system have been determined. A specific interaction energy parameter, ΔA_j, for each step of ligand exchange of thiocyanate for iodide or cyanide is calculated according to the quasi-lattice theoretical formalism. In the iodide system both complexing steps are described by almost equal total interaction energies with an average value $\Delta A = -7.8$ kJ·mol^{-1}. In the cyanide system the second complex is dominating, giving the following sequence for the calculated total interaction energies: ($\Delta A_2 = -26.0$ kJ·mol^{-1}) < ($\Delta A_1 = -22.0$ kJ·mol^{-1}) < ($\Delta A_3 = -12.5$ kJ·mol^{-1}). This sequence may be caused by a coordination change in the second or third step of association. The difference in values in ΔA_1 is in accordance with the softness order $CN^- > I^- > SCN^-$, indicating that the pure Coulomb contribution to the interaction energies is of minor importance.

Introduction

In a recent investigation on complex formation between polyvalent metal ions and fluoride in molten KSCN,[1] we proposed that the change in quasi-lattice total interaction energy,[2] ΔA, for the ligand-exchange reaction

$$\text{M–NCS} + F^- \rightarrow \text{M–F} + SCN^- \qquad (1)$$

might be formally looked upon as a sum of two contributions according to

$$\Delta A = \Delta A_{\text{Coulomb}} + \Delta A_{\text{soft}} \qquad (2)$$

In these typical hard acceptor–hard donor systems the most important contribution to the complex formation is considered to be the change in hard-sphere Coulomb interaction energy, $\Delta A_{\text{Coulomb}}$, on replacing a thiocyanate ion by the smaller fluoride ion in the coordination sphere of the polyvalent metal ion. ΔA_{soft} was introduced to account for small contributions from covalent interaction between the metal ion and the *nitrogen* end of the thiocyanate ion, essentially counteracting the ligand exchange (1).

The present investigation was undertaken to elucidate the complexation in typical soft acceptor–soft donor systems, where the situation should be quite different. Silver was chosen as a suitable soft acceptor, since Ag^+ added as AgSCN is known to be stable in molten KSCN[3] and silver activities are easily and accurately measured potentiometrically.[4,5] Furthermore, silver(I) is expected to coordinate SCN^- via the soft sulfur atom. The change in hard-sphere Coulomb interaction for the ligand-exchange reaction

$$\text{Ag–SCN} + L^- \rightarrow \text{Ag–L} + SCN^- \qquad (3)$$

where L stands for a soft donor ion, is expected to be very small on account of the low charge and small difference in size of the cations Ag^+ and K^+. The dominating term in relation 2 should thus be ΔA_{soft}. In order to achieve the ligand exchange (3), the ligand L should preferably be softer than the *sulfur* atom of the thiocyanate ion. From complex formation studies of silver in aqueous solution, where the same explanation for the stability of associated species has been offered, the stability sequence for halide and pseudohalide complexes is $CN^- > I^- > SCN^- > Br^- > Cl^-$.[6]

Table I. Composition, Stoichiometric Unit Volume per Silver Atom, Mass Density, and Linear Absorption Coefficient of the Melts Investigated by X-ray Scattering

	C_K/ M	C_{Ag}/ M	C_{SCN}/ M	$10^{-3}V$/ Å	ρ/ (g·cm^{-3})	μ/ cm^{-1}
KSCN	16.60		16.60	1.80	1.61	15.7
(K,Ag)SCN	15.68	0.92	16.60	1.80	1.68	17.7

Earlier investigations on silver cyanide complexation in molten thiocyanates have been concerned with the formation of only one species, either a first, AgCN,[4] *or* a second complex, $Ag(CN)_2^-$.[7] A reinvestigation of the silver cyanide system together with a study of silver iodide complexation in molten KSCN would thus add to the understanding of the thermodynamics of complex formation in this kind of systems.

The calculation of quasi-lattice total interaction energy changes relies on a knowledge of the coordination number, *Z*, of the acceptor ion in the melt under study. It is also of special interest to establish the coordination mode (S or N) of SCN^- vis-â-vis Ag(I) in the molten KSCN medium. This is a prerequisite for a meaningful interpretation of the specific interaction energy pattern according to eq 2. Structural investigations, employing X-ray scattering techniques, were therefore performed to reveal the silver coordination in the melt.

Experimental Section

Chemicals. All chemicals used were of p.A. quality. KSCN was treated as described previously.[8,9] KI and KCN were dried at 120 °C for at least 24 h. AgSCN was used without further treatment. All chemicals were stored under dry atmosphere prior to use.

X-ray Scattering. KSCN and a mixture of weighed amounts of AgSCN and KSCN were premelted and filtered. Both the pure KSCN melt and the (K,Ag)SCN melt were stable throughout the experiments. The compositions and physical properties of the melts are shown in Table I. The mass densities were determined as described previously.[10]

The scattering measurements were performed by using a Seifert GDS large-angle θ–θ diffractometer with a LiF monochromator of Johanson type. The scattered intensities from the surface of the melts were recorded for $0.65° \leq \theta \leq 58.1°$ in steps of $s = 0.0335$ ($s = 4\pi\lambda^{-1} \sin \theta$). A total of 40 000 counts were collected at each point. The recording of intensity data was repeated once in order to check the reproducibility. Mo Kα radiation ($\lambda = 0.7107$ Å) was used.

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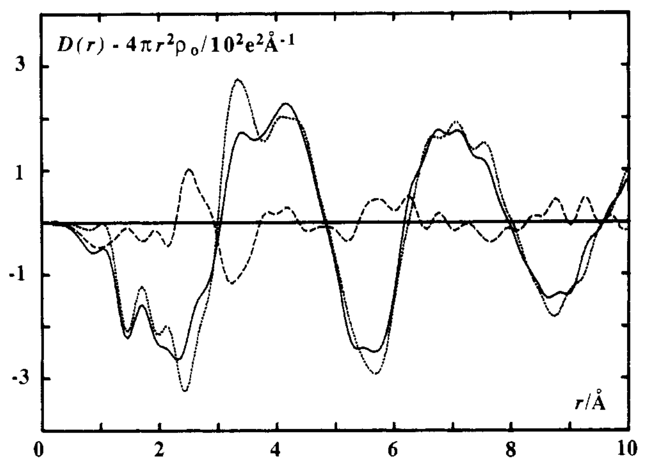

Figure 1. $D(r) - 4\pi r^2\rho_0$ functions: comparison between experimental curves for (K,Ag)SCN melt (—) and pure KSCN melt (···), with the resulting difference curve (- - -). Normalization is according to Table I.

The furnace and temperature control device are described elsewhere.[11] The surface temperature was kept at 187.7 ± 0.3 °C. The data treatment was analogous to that described in ref 12. No correction for multiple scattering was performed due to the relatively high absorption coefficients (see Table I). Data for both melts were normalized to a stoichiometric unit volume V containing one silver atom, referring to the (K,Ag)SCN melt.

Emf Measurements. The following cell was employed to measure the changes in silver activities:

$$\mathrm{Ag}\left|\begin{matrix}\mathrm{KSCN(l)}\\ \mathrm{Ag_2SO_4(satd)}\end{matrix}\right|\left|\begin{matrix}\mathrm{KSCN(l)}\\ \mathrm{AgSCN}\\ \mathrm{KI\ or\ KCN}\end{matrix}\right|\mathrm{Ag}$$

Further details on furnaces, temperature control and cell construction have been given elsewhere.[13-15]

AgSCN–KSCN test melts were prepared and left with stirring for at least 15 h before the complex formation study was started. KI or KCN was then added in portions. Stable emf readings could be obtained within 0.5–3 h after the melt composition had been changed, the time depending on the amount of salt added. Due to the slow dissolution of KI and KCN, each experimental run had to be performed for up to 3 successive days.

Measurements were made at several silver ion concentrations in both systems. The ranges of total concentrations covered in the iodide system were $2.8 \times 10^{-3} < C_{\mathrm{Ag}}/(\mathrm{mol{\cdot}kg^{-1}}) < 8.9 \times 10^{-3}$ and $2.3 \times 10^{-3} < C_{\mathrm{I}}/(\mathrm{mol{\cdot}kg^{-1}}) < 5.0 \times 10^{-1}$. The corresponding figures for the cyanide system were $3.1 \times 10^{-3} < C_{\mathrm{Ag}}/(\mathrm{mol{\cdot}kg^{-1}}) < 9.1 \times 10^{-3}$ and $1.3 \times 10^{-3} < C_{\mathrm{CN}}/(\mathrm{mol{\cdot}kg^{-1}}) < 6.0 \times 10^{-1}$.

Results and Discussion

X-ray Scattering Experiments. Two melts were investigated, pure KSCN and a mixed (K,Ag)SCN melt with a silver concentration of 0.92 M. Experimental radial distribution functions (RDFs) for the two melts together with their difference are displayed in Figure 1. The major change on replacing K^+ by Ag^+ is shown by the difference curve. A peak at 2.6 Å, indicative of a silver–sulfur interaction,[16,17] is followed by a dip at 3.2 Å, a distance close to the potassium–sulfur one in solid KSCN.[18] Model calculations and a preliminary least-squares refinement of interatomic distance parameters were made using data for the pure KSCN melt in order to get a starting point for the analysis of data pertaining to the (K,Ag)SCN melt. Only interactions shorter than approximately 3.5 Å were taken into account, since

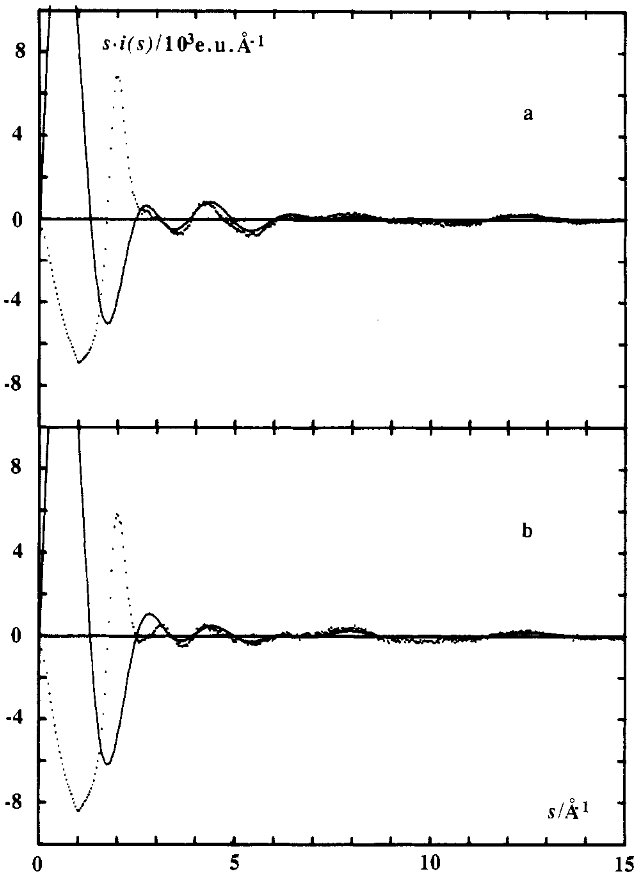

Figure 2. Observed (dots) and calculated (—) $s[i(s)]$ functions for (a) pure KSCN melt and (b) (K,Ag)SCN melt. Parameters used are given in Tables I and II.

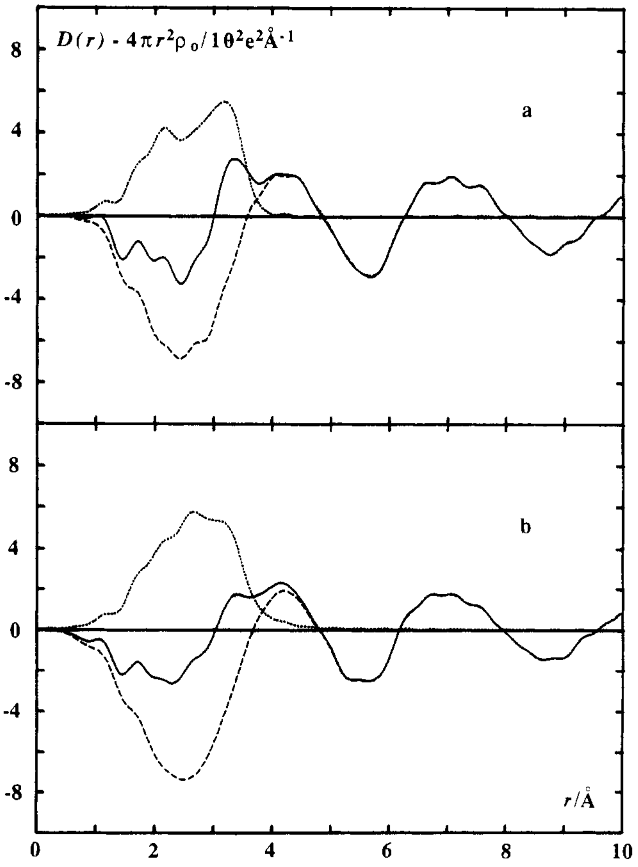

Figure 3. Experimental (—) and modeled (···) $D(r) - 4\pi r^2\rho_0$ curves and their differences (- - -) for (a) pure KSCN melt and (b) (K,Ag)SCN melt. Parameters used are given in Tables I and II.

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Table II. Parameters Used for Calculation of the Theoretical Curves in Figures 2 and 3[a]

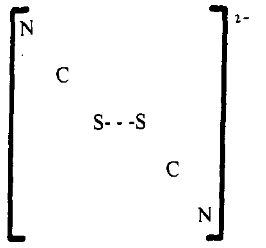
	KSCN			(K,Ag)SCN		
	d/Å	b/Å^2	n	d/Å	b/Å^2	n
Ag–S				2.57 (1)	0.021 (3)	4.2 (3)[d]
K–S	3.24	0.021	1.1[b]	3.24 (1)	0.026 (3)	1.3 (1)[b]
K–N	2.54	0.027	1.4[b]	2.51 (2)	0.017 (4)	1.3 (1)[b]
K–C	2.90	0.038	1.3[b]	2.92 (3)	0.031 (6)	1.4 (2)[b]
S–S	2.06	0.022	1.1[c]	2.02 (1)	0.021 (2)	1.1 (1)[c]
S–N	2.78	0.010	1.0	2.78	0.018 (4)	1.0
S–C	1.63	0.0006	1.0	1.63	0.0006	1.0
C–N	1.15	0.0006	1.0	1.15	0.0006	1.0

[a] d = interatomic distance, b = temperature coefficient, and n = number of interactions. The data given for pure KSCN melt are from a preliminary refinement and were used as a starting point for the refinement of the (K,Ag)SCN melt. Refined parameters are given with one mean error in brackets. [b] Per K atom. [c] Per S atom. [d] Per Ag atom.

the aim of the investigation was to reveal the coordination mode and the distance and number of interactions of silver solvated by thiocyanate and thus not to provide a detailed structure analysis of molten KSCN. The two first peaks in the RDF for pure KSCN are due to internal interactions, C–N at 1.15 Å and S–C at 1.63 Å, within the thiocyanate ion.[19] These distances, the number of interactions (1.0) per SCN$^-$ and a reasonable value of the temperature coefficients b (0.0006 Å^2) were not refined. The refinements were carried out in the interval $3.0 < s/\text{Å}^{-1} < 15.0$. Experimental and modeled curves are displayed in Figures 2 and 3. The results of the calculations are given in Table II.

The data analysis yields an Ag–S distance of 2.57 Å and a coordination number of 4. The observed Ag–S distance of 2.57 Å is significantly larger than the crystal structure value of 2.47 Å reported for a distance AgSCN molecule in $NH_4Ag(SCN)_2$,[16] whereas it agrees with the Ag–S distance of 2.581 Å for tetrahedrally coordinated silver in (thiocyanato)bis(triphenylphosphine)silver(I),[17] suggesting a tetrahedral arrangement of SCN$^-$ around silver in the thiocyanate melts. The refined parameters of the average closest potassium–thiocyanate interactions show a lower number of nearest neighbors and shorter distances as compared to the crystal structure of KSCN.[18] Further comparison with the crystal structure cannot be made by using our simple model, whose purpose is only to serve an aid in revealing silver–thiocyanate coordination.

An unexpected feature, deserving a few comments, is the appearance of a peak in both RDFs at approx 2 Å, which cannot be explained by an internal interaction within the thiocyanate ion or by a potassium–thiocyanate interaction. Yet, this contribution to the RDF is clearly exposed in our two scattering experiments as well as in earlier neutron diffraction work on molten NaSCN and KSCN.[19] A close look at the radial distribution function from X-ray scattering experiments on molten CsSCN also reveals a small peak at this distance.[20] The tentative assignment, made in our model calculations, of a sulfur–sulfur interaction emerging from a structure unit like



is supported by the prediction of associated species to explain the unusual surface properties of molten KSCN.[21] The associated anion arrangement might also be seen as a precursor of both oxidation and reduction products of molten KSCN.[22-24] When KSCN is electrolytically oxidized, the initial product is $(SCN)_2$, which has essentially the same structure and bond distances as the above species.[25,26] The reduction products, polysulfide ions and cyanide ions, could be achieved by breaking the carbon–sulfur bonds. It should be emphasized here, though, that no traces of oxidation or reduction products could be observed in the investigated melts. The sulfur–sulfur interaction proposed by us to account for the contribution to the RDFs at 2 Å, should emerge from intact associated thiocyanate ions.

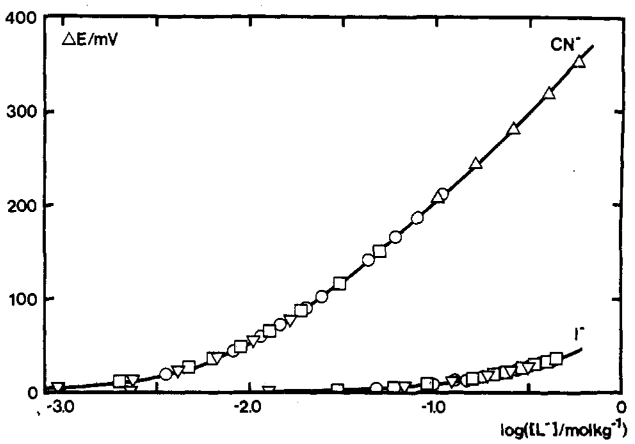


Figure 4. Typical experimental results from emf measurements at 185 °C of the silver activity in AgSCN–KSCN melts containing cyanide and iodide. Measured emf changes from different experimental runs in both systems are displayed. Full-drawn curves are constructed from the stability constants given in Table III by the use of eq 10.

Potentiometric Measurements. The emf of the silver electrode cell can be expressed as

$$E = E_0 + k \log ([Ag^+]/(mol \cdot kg^{-1})) \qquad (4)$$

where $[Ag^+]$ is the concentration of free silver(I), i.e. Ag^+ coordinated by four thiocyanate ions. From calibration measurements in AgSCN–KSCN melts a value of 87.7 ± 0.5 mV for the slope, k, was obtained. This is about 97% of the theoretical value, $RTF^{-1} \ln 10$ at 185 °C, in accordance with previous results.[4,5]

The change in emf when a complexing ligand is added is expressed by

$$\Delta E = E(C_L{=}0) - E(C_L{\neq}0) = k \log (C_{Ag}/[Ag^+]) \qquad (5)$$

C_L is the total concentration of I$^-$ or CN$^-$ and C_{Ag} is the total concentration of Ag^+. The experimental results are displayed in Figure 4. For each system, data points with the same marker symbol define measurements performed at the same C_{Ag}. It is clear that in both systems the change in emf is insensitive to variations in total silver concentration, inferring that polynuclear complexes do not have to be taken into account in the data treatment.

The complexation can thus be described by a set of equilibria, comprising mononuclear complexes only

$$Ag^+ + jL^- \rightleftharpoons AgL_j^{1-j} \qquad (6)$$

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Table III. Overall Stability Constants for $Ag(CN)_j^{1-j}$ and AgI_j^{1-j} in Molten KSCN and Molten Equimolar $(K,Na)NO_3$[a]

Silver Cyanide Complexes

	this work	ref 4	ref 7	ref 28[b]
$\beta_1/(mol^{-1}\cdot kg)$	$(1.26 \pm 0.03) \times 10^2$	1.7×10^2		$(1.5 \pm 0.8) \times 10^4$
$\beta_2/(mol^{-2}\cdot kg^2)$	$(1.74 \pm 0.02) \times 10^4$		4.1×10^4	$(6.2 \pm 0.6) \times 10^9$
$\beta_3/(mol^{-3}\cdot kg^3)$	$(2.52 \pm 0.10) \times 10^4$			$(9.3 \pm 3.1) \times 10^{12}$
solvent melt	KSCN	KSCN	KSCN	$(K,Na)NO_3$
$t/°C$	185	174–204	195	246

Silver Iodide Complexes

	this work	ref 27	ref 13
$\beta_1/(mol^{-1}\cdot kg)$	2.62 ± 0.03	4.2×10^3	
$\beta_2/(mol^{-2}\cdot kg^2)$	2.41 ± 0.08		3.1×10^6
$\beta_3/(mol^{-3}\cdot kg^3)$			2.27×10^7
$\beta_4/(mol^{-4}\cdot kg^4)$			2.8×10^6
solvent melt	KSCN	$(K,Na)NO_3$	$(K,Na)NO_3$
$t/°C$	185	280	280

[a] The error limits define a 95% confidence interval. [b] Recalculated values (see text).

where the coordinated thiocyanate ions have been omitted for the sake of clarity. The cumulative and stepwise association constants are expressed through

$$\beta_j = \frac{[AgL_j^{1-j}]}{[Ag^+][L^-]^j} \tag{7}$$

$$K_j = \frac{[AgL_j^{1-j}]}{[AgL_{j-1}^{2-j}][L^-]} \tag{8}$$

Association constants were calculated, from 28 (C_{Ag}, C_I, ΔE) points in the iodide system and 31 (C_{Ag}, C_{CN}, ΔE) points in the cyanide system, by a recently described least-squares method.[9] Complex formation constants (Table III) for two and three consecutive steps could be obtained for the iodide and cyanide systems, respectively.

Combining eq 5 with the stoichiometric requirement

$$C_{Ag} = [Ag^+](1 + \sum_{j=1}^{2\text{ or }3} \beta_j[L^-]^j) \tag{9}$$

yields

$$\Delta E = k \log (1 + \sum_{j=1}^{2\text{ or }3} \beta_j[L^-]^j) \tag{10}$$

Equation 10 was used to construct the solid lines in Figure 1, with β values taken from Table III.

In exploratory experiments the ability of Cl^- and Br^- to form complexes with Ag^+ was investigated. No change in silver activity of a (K^+, Ag^+)–(SCN^-) melt could be detected even when KCl and KBr were added in amounts corresponding to concentrations as high as 0.5 $mol\cdot kg^{-1}$. It is thus concluded that the stability sequence for silver halide and pseudohalide complexes, $CN^- > I^- > SCN^- > Br^- > Cl^-$, in aqueous solution is parallel in molten KSCN, although no distinction can be made between chloride and bromide from our measurements.

The fraction α_j of different iodide and cyanide complexes is defined as

$$\alpha_j = [AgL_j^{1-j}]/C_{Ag} \tag{11}$$

Here α_0 is the fraction of $Ag(SCN)_4^{3-}$. From Figure 5 it is clear that in the iodide system no complex dominates at any iodide concentration. The cyanide system offers a different picture with one complex, $Ag(CN)_2^-$, as the dominating species in most parts of the free-ligand concentration range. Obviously, the iodide complexation is so weak that a similar stability pattern cannot be revealed within the concentration range investigated here.

The quasi-lattice theory,[2] applied to complex formation in reciprocal molten salt mixtures, expresses total acceptor–donor interaction energy changes, including free energy contributions from changes in internal degrees of freedom of polyatomic ions, for ligand-exchange reactions like

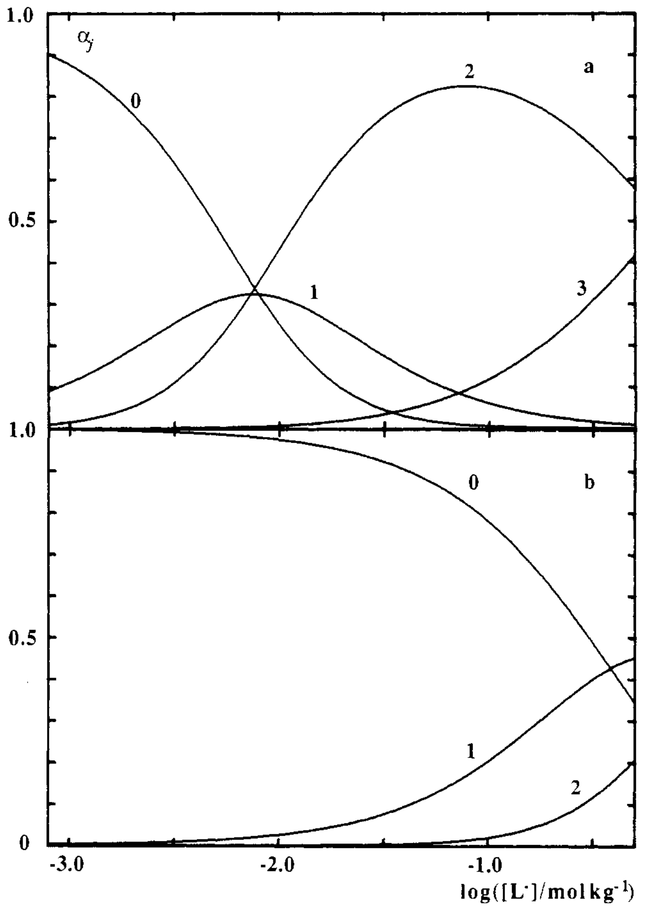

Figure 5. The fraction α_j of Ag in complexes (a) $Ag(CN)_j^{1-j}$ and (b) AgI_j^{1-j} in molten KSCN at 185 °C. j is indicated on the curves.

$$Ag(SCN)_{5-j}L_{j-1}^{3-} + L^- \rightarrow Ag(SCN)_{4-j}L_j^{3-} + SCN^- \tag{12}$$

through a set of parameters ΔA_j. Once the stepwise association constants, K_j, are known, ΔA_j for all steps of ligand exchange can be calculated. For the first step, for instance, the general expression is[2]

$$K_1 = Z[\exp(-\Delta A_1/RT) - 1] \tag{13}$$

Here K_1 is expressed in mole fraction units and Z is the quasi-lattice coordination number.

In view of the results obtained in the X-ray scattering experiments, a value of 4 for Z is used for the calculation of total specific interaction energies for the two complex systems. Results of the calculations are given in Table IV. In the iodide system the values of ΔA_1 and ΔA_2 are almost equal. Thus, no evidence is found for any deviation from the general quasi-lattice assumptions, i.e. that the complexation proceeds as a single ligand exchange (eq 3) in both steps. In the cyanide system, however, the dominance of the second complex is clearly reflected in the following sequence which is obtained for the total interaction energies:

$$\Delta A_2 \lesssim \Delta A_1 \ll \Delta A_3 \tag{14}$$

Thus, the apparent high stability of $Ag(CN)_2^-$ is not due to a thermodynamically favorable formation process

$$AgCN + CN^- \rightarrow Ag(CN)_2^- \tag{15}$$

but rather to a pronounced destabilization of $Ag(CN)_3^{2-}$. One hypothesis to account for this is that a complete desolvation of Ag(I) occurs at the second or third step of cyanide association. This means that the progressive complexation actually proceeds via a sequence of species that are best described as $Ag(SCN)_4^{3-}$–$AgCN(SCN)_3^{3-}$–$Ag(CN)_2^-$ or $Ag(CN)_2(SCN)_2^{3-}$–$Ag(CN)_3^{2-}$. If so, the calculated parameter values for ΔA_3 and

Table IV. Specific Interaction Energies, Calculated for the Ligand-Exchange Reactions

$$Ag(SCN)_{5-j}L_{j-1}^{3-} + L^- \rightarrow Ag(SCN)_{4-j}L_j^{3-} + SCN^-$$

$$Ag(NO_3)_{5-j}L_{j-1}^{3-} + L^- \rightarrow Ag(NO_3)_{4-j}L_j^{3-} + NO_3^-$$

in Molten KSCN and Equimolar (K,Na)NO_3[a]

Silver Cyanide Complexes

	this work	ref 28[b]
$-\Delta A_1/(kJ \cdot mol^{-1})$	22.0 ± 0.1	46
$-\Delta A_2/(kJ \cdot mol^{-1})$	26.0 ± 0.1	64
$-\Delta A_3/(kJ \cdot mol^{-1})$	12.9 ± 0.2	44
solvent melt	KSCN	(K,Na)NO_3
t/°C	185	246

Silver Iodide Complexes

	this work	ref 13 and 27
$-\Delta A_1/(kJ \cdot mol^{-1})$	7.7 ± 0.1	43
$-\Delta A_2/(kJ \cdot mol^{-1})$	7.9 ± 0.1	39
$-\Delta A_3/(kJ \cdot mol^{-1})$		11
solvent melt	KSCN	(K,Na)NO_3
t/°C	185	280

[a] The error limits define a 95% confidence interval. [b] From recalculated stability constants (see text).

possibly ΔA_2 would of course have no physical meaning. Nevertheless, the calculation as such is useful, since it reveals a thermodynamic pattern, which is clearly different from that exhibited by the previously investigated systems of hard–hard character in liquid KSCN.[1,9]

The observed difference in ΔA_1 for the two systems is in accordance with the softness order $CN^- > I^- > SCN^-$, indicating that the interactions between the anions are of essentially covalent nature, the pure Coulomb contributions to ΔA being of little importance.

Comparison between findings of this study and silver cyanide and silver iodide complexation results obtained in molten (K,Na)NO_3 reveals similarities in the behavior of the stepwise complex formation process. To visualize this, average ligand numbers, $\bar{n}$, were plotted as a function of free ligand concentration. The ligand numbers were calculated according to

$$\bar{n} = \frac{\sum_{j=1}^{2\text{ or }3} j\beta_j[L^-]^j}{1 + \sum_{j=1}^{2\text{ or }3} \beta_j[L^-]^j} \qquad (16)$$

Association constants used for the calculation are collected in Table III. The values used for the (Ag, K, Na)–(CN, NO_3) system were recalculated from the experimental data given in ref 28 by using our least-squares treatment, which minimizes the sum $\sum(\Delta E_{\text{exptl}} - \Delta E_{\text{calcd}})^2$, ΔE_{calcd} being calculated according to eq 10. It was found that the existence of a polynuclear complex, Ag_2CN^+, predicted from the original graphical evaluation of association constants, could not be confirmed. On the other hand, a third complex, $Ag(CN)_3^{2-}$, was clearly established at the lowest temperature, 246 °C, employed in that investigation. Plots for all four complex systems are displayed in Figure 6.

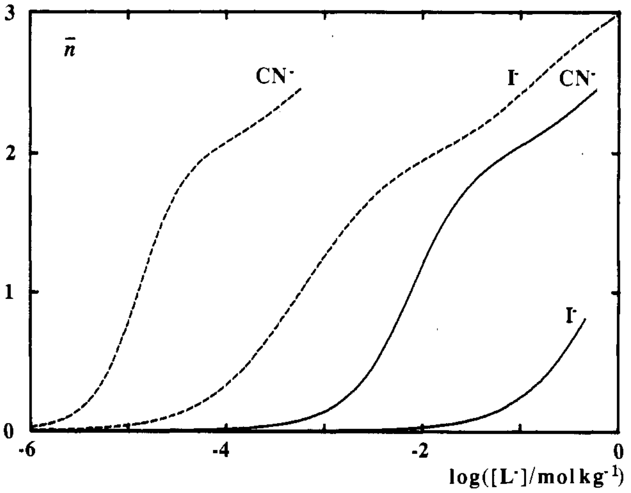

Figure 6. Calculated $\bar{n}$ curves for silver cyanide and silver iodide association in molten KSCN (—) and equimolar (K,Na)NO_3 (---). Average ligand numbers were calculated with stability constants from Table III by the use of eq 16.

As expected, the overall strength of soft acceptor–soft donor interactions is favored by a hard solvent melt like (K,Na)NO_3. This is obvious from Figure 6 by the different ligand concentrations needed to produce a mixture of complex species giving the same $\bar{n}$ in (K,Na)NO_3 and KSCN, even though the temperatures in the systems under comparison are considerably different.

The nearly identical shapes of the formation curves might be taken as an indication that the association process in the different solvent melts proceeds in a similar manner. The formation curves for cyanide complexes in both nitrate and thiocyanate melts clearly show a distinct tendency to a plateau at $\bar{n} = 2$. (There is, however, no direct correspondence to the well-known extreme stability of $Ag(CN)_2^-$ in aqueous solution.) This shape of the formation curves is significantly different from the smooth S-shape, which is characteristic of systems of consecutively formed complexes with all ΔA_j of equal magnitude irrespective of actual step j.

A close inspection of the calculated ΔA_j values of Table IV reveals, however, a remarkable difference in the association energy sequences for the three consecutive cyanide complexation steps. The energy sequence (14) for the molten KSCN solvent is to be compared to

$$\Delta A_2 \ll \Delta A_1 \lesssim \Delta A_3 \qquad (17)$$

for the nitrate medium. The stop at $\bar{n} = 2$ in (K,Na)NO_3 is thus really due to an energetic stabilization of the system in the second net association step (15). If a considerable desolvation of Ag(I) occurs at this step, the two types of ΔA sequences—(14) and (17)—might be ascribed in part to the difference in affinity of Ag(I) for SCN^- and NO_3^-.

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Registry No. $Ag(SCN)_4^{3-}$, 23949-91-9; AgSCN, 1701-93-5; KSCN, 333-20-0; KCN, 151-50-8; KI, 7681-11-0.

Supplementary Material Available: A listing of experimental emf data (2 pages). Ordering information is given on any current masthead page.

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