Equilibrium and Enthalpy Measurements on the Copper(I) and Silver(I) Chloride, Bromide, Iodide and Thiocyanate Systems in Tetrahydrothiophene

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Abstract

Potentiometric and calorimetric measurements have been carried out for the determination of the stability constants and the enthalpy changes of the formation of copper(I) and silver(I) halide and thiocyanate complexes in tetrahydrothiophene (THT). THT is a sulfur donor solvent, which solvates the soft acceptors copper(I) and silver(I) well. THT has a low dielectric constant $\epsilon \approx 8$, which affects the stability constants and the complex distribution, since the solvent has limited ability to neutralize ionic charges. Two mononuclear complexes are formed in all systems. The stabilities of the stepwise silver(I) halide complexes increase in the order $Cl^- < Br^- < I^-$. The stabilities of the first copper(I) halide complexes are almost identical, while the stabilities of the second copper(I) halide complexes follow the sequence $Cl^- > Br^- < I^-$. The neutral complexes of these systems are considerably more stable in THT than in any other previously studied solvent, in spite of the strong solvating properties of THT. This is because the electrostatic forces become predominant in a solvent with a low dielectric constant where charges are neutralized through ion pair formation. The enthalpy changes of the formation of the first complexes are small and negative, except for copper-(I) chloride and iodide where small positive values are found. For all systems, the second complexes are formed in strongly endothermic reactions.

Introduction

In order to study the effect of the solvation on the complex formation, the complex formation thermodynamics for the copper(I) and silver(I) halide and thiocyanate system have been studied in water [1–3], dimethylsulfoxide (DMSO) [4], acetonitrile (AN) [5] and pyridine [6]. In this series of studies, the complex formation thermodynamics of these systems in the sulfur donor solvent tetrahydrothiophene (THT) is reported in this paper.

THT solvates both copper(I) and silver(I) fairly strongly [7, 8]. The free energies of solvation of copper(I) increase in the order water $\leqslant$ THT $<$ DMSO $<$ AN $<$ pyridine, while the heats of solvation increase in the order water $\leqslant$ DMSO $<$ AN $<$ THT $<$ pyridine. The corresponding sequences for silver(I) are water $<$ AN $<$ DMSO $<$ THT $<$ pyridine for both free energies and heats of solvation [7, 8]. This shows the somewhat softer character of silver(I) compared to copper(I), as THT and pyridine are the softest of the studied solvents [9]. A previous Raman spectroscopic study on solvated mercury(II) halides has shown that the Hg–S (THT) bond is stronger than the corresponding Hg–N (pyridine) bond in HgX_2L_2 complexes, L = solvent molecule, in solution and solid state [9, 10]. The heats of solvation of mercury-(II) halides have, however, shown larger values in pyridine than in THT. This is because much more energy is consumed in making solvent molecules available for solvation of metal ions or complexes in THT than in pyridine, due to stronger intermolecular forces in THT [9, 11]. It is therefore reasonable to believe that the Ag–S (THT) bonds are at least as strong as the Ag–N (pyridine) ones in corresponding complexes. This is further supported by silver(I) forming weak complexes with THT in pyridine solution, $K_1 = 0.84$ M^{-1} [12]. The halide and thiocyanate ions are similar and fairly weakly solvated in all aprotic solvents. The chloride and bromide ions are well solvated in protic solvents [7, 8, 13]. In comparison with the conditions prevailing in aqueous solution, copper(I) is favoured, relative to copper(0) and copper(II) in aprotic solvents [7]. Copper(I) is very much favoured in THT, since in fact, copper(II) is spontaneously reduced to copper(I) by THT [14]. This means that copper(I) cannot be oxidized in THT solution. The strong solvation of copper(I) causes the neutral copper(I) halide and thiocyanate complexes, which are slightly soluble in water, to be very soluble in THT.

Complete thermodynamic studies on silver(I) halide systems are only possible in strong donor solvents, such as pyridine and THT, where the neutral silver(I) halides are soluble. Thus large solvation energies are needed to overcome the lattice energies of the silver(I) halides. The solubilities of the neutral silver(I) halides are too low in water, dimethyl-sulfoxide and acetonitrile, due to weak solvation properties of soft acceptor ions such as silver(I), to allow accurate potentiometric and calorimetric studies. Electrochemical studies work surprisingly well in THT in spite of a very low dielectric constant. However, the choice of ionic medium is crucial, since it must be completely dissociated. In this case, tetra-butylammonium tetrafluoroborate works well. The perchlorate is not completely dissociated in THT. Earlier measurements of copper(I) halides in aceto-nitrile were carried out with both tetraethyl-ammonium perchlorate and tetrafluoroborate as ionic medium. Only minor differences in the results were found [5]. The tetrabutylammonium halides and thiocyanate used as sources for the ligand are also completely dissociated in THT [7].

THT is a solvent with a dipole moment of 1.90 D [15], and the dielectric constant is estimated to be around 8. This means that only 1:1 salts can be com-pletely or partly dissociated. Salts very rarely dissociate in solvents with dielectric constants lower than 6 [7]. Previous studies on the complex forma-tion of copper(I) halides have shown that the stability constants decrease with increasing solvation of the copper(I) ion for the first complex and with increasing solvation of the CuX complex for the second complex. It is however uncertain if this tendency persists in a solvent with a very low di-electric constant. It is likely that neutral complexes are especially stable, because the tendency for ion pair formation increases as the electrostatic forces between ions become more predominant.

Experimental

Chemicals

Tetrahydrothiophene (Fluka 97%) was purified and stored over 3 Å molecular sieves as described previously [7].

A copper(I) tetrafluoroborate THT solution was prepared from $Cu(CH_3CN)_4BF_4$. This salt was dissolved in THT and due to the stronger solvation properties of THT the acetonitrile was exchanged. The acetonitrile, which has a lower boiling point than THT, was then distilled off. $Cu(CH_3CN)_4BF_4$ was prepared [16] and handled [5] as described else-where. The copper(I) content in solution was deter-mined by EDTA titration with murexid as indicator. Prior to the titration, the THT was oxidized by the addition of several small portions of concentrated nitric acid, and diluted with water.

$AgClO_4$ (Fluka p.a.) was recrystallized according to Radell *et al.* [17] and kept over P_2O_5 at reduced pressure.

The tetrabutylammonium salts (Fluka p.a.) were recrystallized from acetone and diethylether, and dried over P_2O_5 at reduced pressure.

Copper amalgam containing about 3% copper was prepared as described elsewhere [1].

Potentiometry

The emf values were measured with silver metal and copper amalgam electrodes. The total concentra-tion of metal ion during the titrations was in the range $1 < C_M < 10$ mM. The metal concentration in the reference electrodes was the same as the initial concentration in the measuring electrodes. The ligand solution was added in portions giving total ligand concentrations in the range $0.1 < C_L < 8$ mM. The previously used set-up for potentiometric measure-ments with Ingold vessels connected to each other with salt bridges could not be used due to too high resistance in the medium used. Instead the set-up used was a cell with two compartments, divided with a sintered glass filter which allowed for electrical transport but not for mass transport. The resistance over this cell with 0.1 M Bu_4NBF_4 in THT solution was $1-2$ MΩ compared to about 1 GΩ for an Ingold vessel set up with the same media. The potentials were measured with a 4600 Eldorado digital potentiometer with an input resistance of 1 GΩ. The emf values were reproduced within a few millivolts. The copper amalgam and silver electrodes followed Nernst's law in the range $0.01 < C_M < 10$ mM. A stream of dry oxygen-free nitrogen saturated with THT, of the same activity as in the media used, passed through the solutions during the titrations. The solutions were mechanically stirred during the titrations. The titrations were always completed in one day. No precipitation was found in the studied solutions, but traces of metallic silver were found in silver(I) perchlorate solutions after a few days.

Calorimetry

The titration calorimeter used is described else-where [18]. The calorimeter vessel initially con-tained 40 ml metal ion solution with an initial con-centration in the range $3 < C_M < 10$ mM. The ligand solutions of chloride, bromide and thiocyanate were 20 mM, while only a 5 mM solution of tetrabutylam-monium iodide could be prepared. A total of 20 ml ligand solution was added in each series. If the com-plex formation was not completed, 20 ml was with-drawn and the titration continued. The heats of dilu-tion were negligible in the concentration range used.

Calculations

The stability constants and the enthalpy changes were calculated with the computer program EMK

TABLE I. Overall Stability Constants (β_j (M^{-j})) for the Complex Formation of the Copper(I) Halide and Thiocyanate Complexes in Tetrahydrothiophene Solution at 25 °C. Medium 0.1 M Bu$_4$NBF$_4$. The Limits of Error Refer to Three Standard Deviations; NP Denotes the Number of Observations (emf values measured) for Each System

	Cl⁻	Br⁻	I⁻	SCN⁻
β_1	$(1.013 \pm 0.018) \times 10^7$	$(9.39 \pm 0.30) \times 10^6$	$(9.50 \pm 0.34) \times 10^6$	$(1.012 \pm 0.029) \times 10^6$
β_2	$(1.087 \pm 0.039) \times 10^{10}$	$(6.48 \pm 1.63) \times 10^8$	$(2.39 \pm 1.04) \times 10^9$	$(5.85 \pm 0.54) \times 10^8$
NP	103	99	108	58

TABLE II. Overall Stability Constants (β_j (M^{-j})) for the Complex Formation of the Silver(I) Halide and Thiocyanate Complexes in Tetrahydrothiophene Solution at 25 °C. Medium 0.1 M Bu$_4$NBF$_4$. The Limits of Error Refer to Three Standard Deviations; NP Denotes the Number of Observations (emf values measured) for Each System

	Cl⁻	Br⁻	I⁻	SCN⁻
β_1	$(7.12 \pm 0.36) \times 10^6$	$(4.17 \pm 0.19) \times 10^7$	$(7.28 \pm 0.56) \times 10^7$	$(3.27 \pm 0.04) \times 10^5$
β_2	$(1.44 \pm 0.17) \times 10^{10}$	$(9.18 \pm 0.97) \times 10^{10}$	$(1.87 \pm 0.40) \times 10^{11}$	$(1.27 \pm 0.04) \times 10^8$
NP	79	92	29	200

[19] and KALORI [20], respectively. The stability constants obtained from the potentiometric measurements were used as fixed parameters in the calculations of the enthalpy changes.
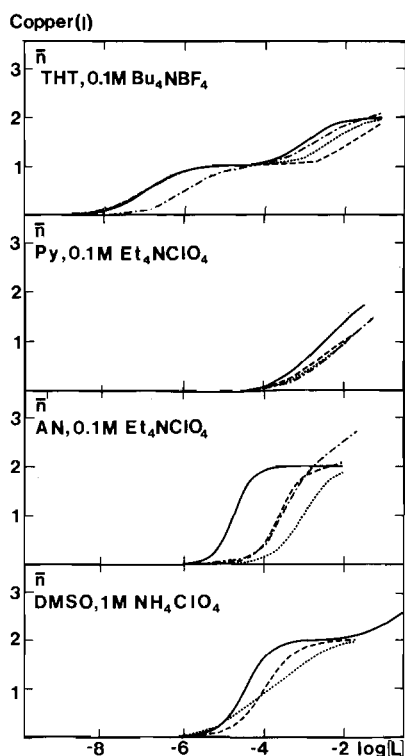
Fig. 1. Complex formation curves of the copper(I) halide and thiocyanate systems in tetrahydrothiophene, pyridine, acetonitrile and dimethylsulfoxide. Chloride, solid line; bromide, dashed; iodide, dotted; thiocyanate, dots and dashes.

Results

The overall stability constants for the copper(I) and silver(I) halides and thiocyanate complexes are given in Tables I and II. (The stepwise stability constants are given in Tables V and VI). The complex formation functions for these systems are given in Figs. 1 and 2. Two mononuclear complexes are found in the studied systems. The stabilities of the first copper(I) halide complexes are almost identical. The second complexes are much weaker than the first ones and the stabilities follow in the order Cl⁻ > Br⁻ < I⁻. The first copper(I) thiocyanate complex is 10 times weaker than the halide complexes in THT. This difference is much smaller in the previously used solvents. The second copper(I) thiocyanate complex is, on the other hand, stronger than corresponding bromide and iodide complexes.
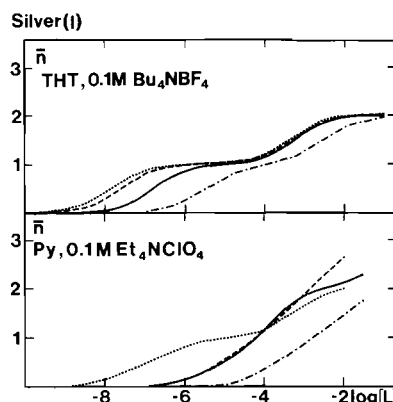

Fig. 2. Complex formation curves of the silver(I) halide and thiocyanate systems in tetrahydrothiophene and pyridine. The symbols are the same as in Fig. 1.

The stabilities of the stepwise silver(I) halide complexes both follow the sequence, $Cl^- < Br^- < I^-$. The stabilities of the second silver(I) halide complexes are almost equal, the difference in log K_2 being only 0.10 between the two extremes chloride and iodide. The silver(I) thiocyanate complexes are significant weaker than the halide complexes, as is also found in pyridine (Table VI and Fig. 2).

TABLE III. Overall Enthalpies ($\Delta H^\circ_{\beta j}$ (kJ mol^{-1})) for the Formation of the Copper(I) Halide and Thiocyanate Complexes in Tetrahydrothiophene Solution Containing 0.1 M Bu$_4$NBF$_4$ as an Ionic Medium at 25 °C. The Limits of Error Refer to Three Standard Deviations; NP Denotes the Number of Observations (aliquots added) for Each System

Ligand	Cl$^-$	Br$^-$	I$^-$	SCN$^-$
$\Delta H^\circ_{\beta 1}$	4.6 ± 1.2	$-(6.2 \pm 1.0)$	4 ± 5	$-(9.8 \pm 1.1)$
$\Delta H^\circ_{\beta 2}$	51.3 ± 3.0	19.0 ± 4.8		$-(3.5 \pm 2.2)$
NP	70	79	46	84

The overall enthalpy changes of the formation of copper(I) and silver(I) halide and thiocyanate complexes are given in Tables III and IV. The enthalpy changes of the first complex show small negative values, except for the copper(I) chloride and iodide complexes where positive values are found. For all systems, the second complexes are formed in strongly endothermic reactions. The thermodynamic functions for the stepwise formation of copper(I) and silver(I) halide and thiocyanate complexes in THT are given in Tables V and VI, as well as corresponding values in pyridine, acetonitrile and DMSO.

Discussion

The complex formation thermodynamics for copper(I) and silver(I) halide and thiocyanate systems in THT, pyridine, acetonitrile and DMSO, given in Tables V and VI, show that the stabilities of the complexes are exceptionally high in THT. In previously studied solvents, the stabilities of the first and second complexes are shown to be inversely proportional to the solvation of the copper(I) ion and the CuX
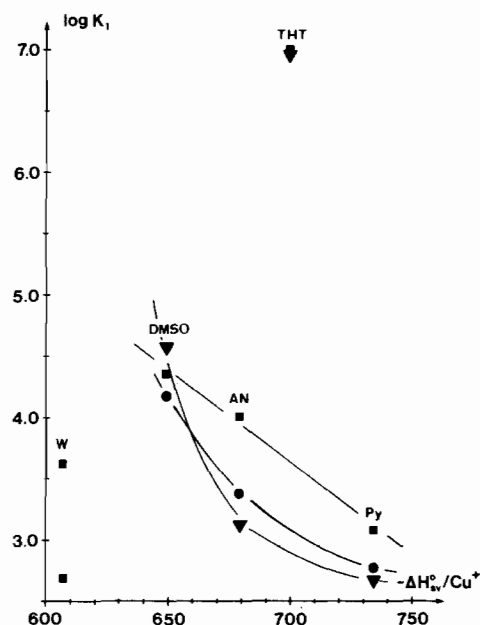

Fig. 3. The stability constants of the first copper(I) halide complexes are plotted against heat of solvation of the copper-(I) ion $-\Delta H^\circ_{sv}$, for dimethylsulfoxide (DMSO), acetonitrile (AN), tetrahydrothiophene (THT) and pyridine (Py). ■, ● and ▼ denote chloride, bromide and iodide complexes, respectively.

complex, respectively, as can be seen in Figs. 3 and 4. The stabilities of the first copper(I) halide complexes are ten to the power of 3–4 stronger in THT than expected from the heat of solvation of the copper(I) ion in other solvents, Fig. 3. On the other hand the stabilities of the second copper(I) halide complexes in THT are as expected from the heats of solvation of the CuX complexes, Fig. 4. The extraordinary stabilities of the neutral copper(I) halide complexes can be explained by the neutralization of charges through ion pair formation that takes place because the electrostatic forces between ions of different charge that will be predominant in solvents with low dielectric constants. Such solvents have a limited ability to neutralize charges on ions and strong dipoles. A tendency for ion pair formation due to low dielectric constants is not normally seen in solvents with $\epsilon > 10$. On the other hand, salts very rarely

TABLE IV. Overall Enthalpies ($\Delta H^\circ_{\beta j}$(kJ mol^{-1})) for the Formation of Silver(I) Halide and Thiocyanate Complexes in Tetrahydrothiophene Solution Containing 0.1 M Bu$_4$NBF$_4$ as an Ionic Medium at 25 °C. The Limits of Error Refer to Three Standard Deviations; NP Denotes the Number of Observations (aliquots added) for Each System

Ligand	Cl$^-$	Br$^-$	I$^-$	SCN$^-$
$\Delta H^\circ_{\beta 1}$	$-(4.8 \pm 1.4)$	$-(13.7 \pm 1.6)$	$-(17.7 \pm 4.0)$	$-(11.2 \pm 1.3)$
$\Delta H^\circ_{\beta 2}$	22.8 ± 2.5	8.5 ± 2.8	3.2 ± 6.8	$-(3.5 \pm 2.9)$
NP	76	68	74	88

TABLE V. Equilibrium Constants (K_j (M^{-1})) and Thermodynamic Functions [ΔG_j°, ΔH_j° (kJ mol^{-1}); ΔS_j° (JK^{-1} mol^{-1})] for the Stepwise Formation of Copper(I) Halide and Thiocyanate Complexes in Tetrahydrothiophene (THT), Pyridine and Acetonitrile Containing 0.1 M Ionic Medium at 25 °C

	THT (0.1 M Bu$_4$NBF$_4$)				Pyridine (0.1 M Et$_4$ClO$_4$)[a]				Acetonitrile (0.1 M Et$_4$NCl)				DMSO (1 M NH$_4$ClO$_4$)[c]		
	Cl⁻	Br⁻	I⁻	SCN⁻	Cl⁻	Br⁻	I⁻	SCN⁻	Cl⁻	Br⁻	I⁻	SCN⁻	Cl⁻	Br⁻	I⁻
$\log K_1$	7.005	6.97	6.98	6.01	3.09	2.78	2.69	2.62	4.02	3.39	3.13	3.53	4.37	4.19	4.59
$\log K_2$	3.031	1.84	2.40	2.76	1.91	1.10	0.89	1.21	5.53	3.82	2.84	3.54	4.50	3.75	2.99
$\log K_3$												2.05	0.58		
K_1/K_2	9.43 × 10³	136 × 10³	37.8 × 10³	1.75 × 10³	15	48	64	255	0.03	0.37	1.93	0.95	0.7	2.8	40
$-\Delta G_1^\circ$	40.0	39.8	39.8	34.3	17.6	15.9	15.4	15.0	22.9	19.3	17.8	20.2	24.9	23.9	26.2
$-\Delta G_2^\circ$	17.2	10.5	13.7	15.8	10.9	6.3	5.1	6.9	31.6	21.8	16.2	20.3	25.7	21.7	17.1
$-\Delta G_3^\circ$												11.7			
$-\Delta H_1^\circ$	-4.6	6.2	4	9.8	-13.0	-10.2	-8.5	-4.7	-16.8	-10.5	-8.5	+5.4	6.4	9.3	13.9
$-\Delta H_2^\circ$	-46.7	-25.1		-6.3	-17.3	-20.0		-6.8	-4.4	-16.7	-12.8	-6.0	7.8	-2.1	-3.6
ΔS_1°	150	113	120	82	103	87	80	66	133	100	88	50	62	49	41
ΔS_2°	214	119		74	95	88		46	121	129	97	88	60	78	69
$-\Delta G_{\beta 2}^\circ$	57.2	50.3	53.5	50.0	28.5	22.1	20.5	21.9	54.5	41.1	34.1	40.4	50.6	45.6	43.3
$-\Delta H_{\beta 2}^\circ$	51.3	-19.0		3.5	-30.9	-30.2		-11.6	-21.2	-27.2	-21.3	-0.6	14.2	7.2	10.3
$\Delta S_{\beta 2}^\circ$	364	232		156	197	175		112	254	229	186	137	122	127	110

[a]Ref. 6.   [b]Ref. 5.   [c]Ref. 4. Recalculated values, for I⁻; only CuI and CuI$_2^-$ complexes are formed in DMSO.
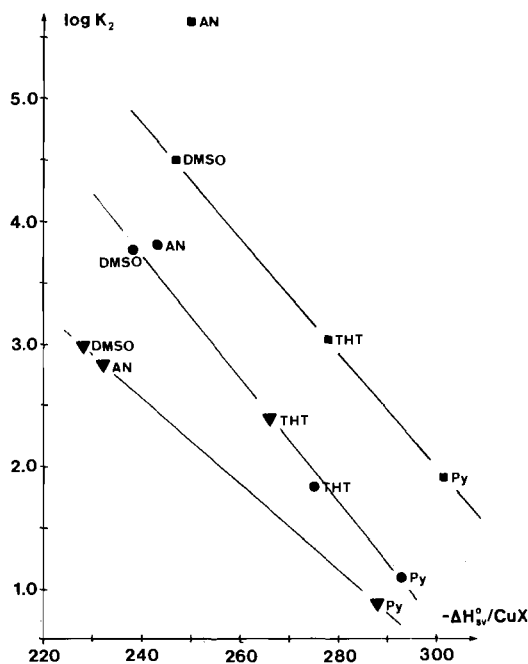
Fig. 4. The stability constants of the formation of the second copper(I) halide complexes are plotted against the heat of solvation of the neutral copper(I) halides, $-\Delta H^\circ_{sv}$. The symbols are the same as in Fig. 3.
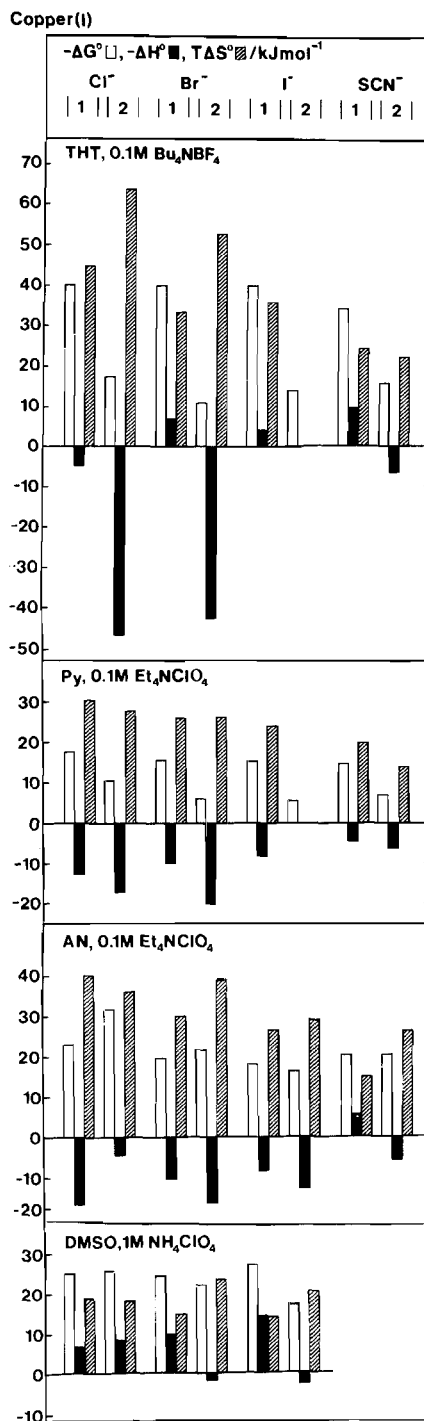

Fig. 5. Stepwise changes of free energy, enthalpy and entropy for the copper(I) halide and thiocyanate systems in tetrahydrothiophene (THT), pyridine (Py), acetonitrile and dimethylsulfoxide (DMSO) at 25 °C.

become slightly more weakly coordinated. At the formation of the second complex a substantial desolvation takes place and no THT molecules remain coordinated to copper(I). The thermodynamic pattern for the formation of the silver(I) halide complexes is similar to that of the copper(I) halides. The first silver(I) halide complexes are formed in exothermic reactions with $-\Delta H^\circ_1$ values increasing in the order $Cl^- < Br^- < I^-$, Table VI. This shows the increasing covalency in the Ag—X bonds. This is less pronounced in copper(I) halide systems since copper(I) is a harder acceptor than silver(I).

The total entropy gain for the two complexes, $\Delta S^\circ_{\beta 2}$, is larger in THT than in pyridine, in spite of pyridine being less ordered than THT, and that the strength of the solvate bonds are similar in pyridine and THT. Furthermore, the $\Delta S^\circ_{\beta 2}$ values are slightly more positive for the copper(I) halide systems than for corresponding silver(I) complexes in THT, while the $\Delta S^\circ_{\beta 2}$ values are equal for the copper(I) and silver(I) halide systems in pyridine, Tables V and VI, Figs. 5 and 6. THT solvates charged species very poorly [7], and one can assume that there are no THT molecules coordinated in the inner coordination sphere of the CuX_2^- and AgX_2^- complexes in THT solution. There probably are solvent molecules in the inner coordination sphere of the MX_2^- complexes in the other solvents studied, since they solvate negatively charged complexes more strongly. Since

the copper(I) ion is more strongly solvated than the silver(I) ion, one can assume that the total entropy change will be larger for the copper(I) systems if the
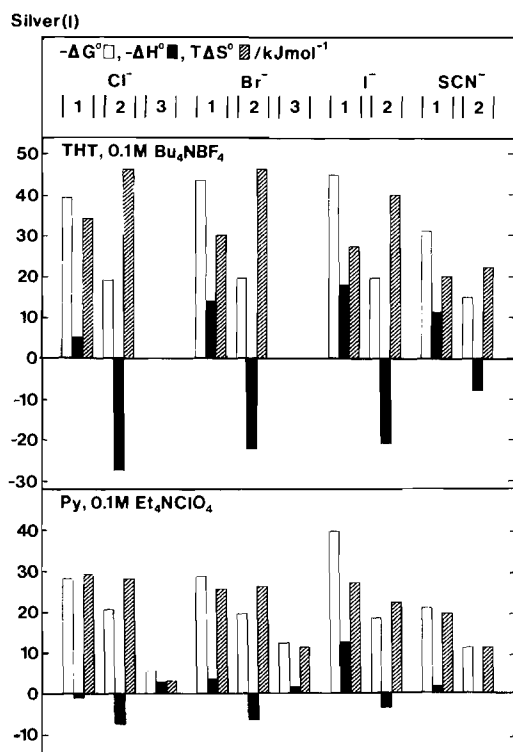
Silver(I)

Fig. 6. Stepwise changes of free energy, enthalpy and entropy for the silver(I) halide and thiocyanate systems in tetra-hydrothiophene (THT) and pyridine (Py) at 25 °C.

lower stability constant than the chloride and iodide complexes. The $AgBr_2^-$ complex is however no less stable than the chloride and iodide complexes. This is probably due to the Ag–Br bonds being stronger because of a higher degree of covalency and more difficult to influence.

Acknowledgement

CuX_2^- and AgX_2^- complexes are equally solvated. It is reasonable to assume that the solvation of the CuX_2^- and AgX_2^- complexes is weak in THT. This supports the fact that there are no THT molecules in the inner coordination sphere of the CuX_2^- and AgX_2^- complexes in THT, while most probably there are pyridine molecules in the inner coordination sphere in these complexes. This also implies that the AgX_2^- complexes are stronger solvated in pyridine than the CuX_2^- complexes. This is due to a higher degree of covalency in the Ag–N (pyridine) bonds than in the corresponding Cu–N ones.

A previous study of the heats of solvation of the mercury(II) halides has shown that the bromide complex is more strongly solvated in THT than the chloride and iodide complexes [11]. This stronger solvation of bromide complexes in THT solutions is well shown by the $CuBr_2^-$ complex, which has a

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