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A CALORIMETRIC STUDY OF THE SILVER (I) COMPLEXES OF SOME SULFUR-CONTAINING AMINES

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ABSTRACT

The enthalpies of the reactions in 0.5 M KNO_3 at 25 °C between the hydrogen and silver(I) ions and a number of sulfur-containing amines of the general formula $R'–S–(CH_2)_nNR_2$ where

$$R' = CH_3, C_2H_5, nC_3H_7, (CH_3)_3C, HOCH_2CH_2, R = H, CH_3, C_2H_5, (CH(CH_3)_2$$

and $n = 2,3$ have been determined by means of direct calorimetric titrations. By use of the ΔG values reported elsewhere, the corresponding ΔS values have been calculated. The complex formation in acid, neutral and alkaline medium is discussed.

INTRODUCTION

The protonation constants of a number of S-containing amines and the stability constants of their complexes with Ag(I) at 25 °C in 0.5 M KNO_3 have been reported in an earlier paper[1]. The general formula of these ligands is $R'–S–(CH_2)_nNR_2$ where

$$R' = CH_3, C_2H_5, nC_3H_7, (CH_3)_3C, HOCH_2CH_2,$$
$$R = H, CH_3, C_2H_5, CH(CH_3)_2, \text{ and } n = 2,3.$$

In acid medium, the complexes $(Ag(LH)_2)^{3+}$ and $(Ag(LH))^{2+}$ were found, in neutral medium $(Ag(LH)L)^{2+}$, and in alkaline medium the four species $(AgL_2)^+$, $(AgL)^+$, $(Ag_2L_2)^{2+}$ and $(Ag_2L)^{2+}$. In acid medium coordination occurs through the S atom, while in alkaline medium chelation occurs in the $(AgL)^+$ and $(AgL_2)^+$ species through the N and S atom.

In order to obtain more information about the complex formation, the enthalpy and entropy changes accompanying the protonation of the ligands and the formation of complexes are now reported from thermometric titrations.

EXPERIMENTAL

Reagents

The ligands used are listed in Table 1. Their synthesis and purification have been reported earlier[1]. All other reagents were analytical grade. All solutions were made up to an ionic strength of 0.5 M KNO_3.

TABLE 1

Ligand	*Formula*	*Abbr.*
2-Aminoethyl methyl sulfide	$CH_3–S–CH_2CH_2NH_2$	AEMS
2-Aminoethyl ethyl sulfide	$C_2H_5–S–CH_2CH_2NH_2$	AEES
2-Aminoethyl propyl sulfide	$CH_3CH_2CH_2–S–CH_2CH_2NH_2$	AEPS
2-Aminoethyl tert. butyl sulfide	$(CH_3)_3C–S–CH_2CH_2NH_2$	AEBS
3-Aminopropyl methyl sulfide	$CH_3–S–CH_2CH_2CH_2NH_2$	APMS
2-Hydroxyethyl 2'-aminoethyl sulfide	$HOCH_2CH_2–S–CH_2CH_2NH_2$	HAS
2-Dimethylaminoethyl methyl sulfide	$CH_3–S–CH_2CH_2N(CH_3)_2$	DMAMS
2-Diethylaminoethyl methyl sulfide	$CH_3–S–CH_2CH_2N(C_2H_5)_2$	DEAMS
2-Diisopropylaminoethyl methyl sulfide	$CH_3–S–CH_2CH_2N(CH(CH_3)_2)_2$	DPAMS

Apparatus

Calorimetric measurements were carried out with an LKB 8700-2 Precision Calorimeter. The titrant was added with an automatical piston buret Tacussel Electroburap, equipped with a preselection unit. With the piston buret, it was possible to regulate the addition speed so that the addition time was almost equal to the heating time in the calibration experiment.

The calculations were performed with a number of Fortran computer programmes, and executed on a Varian 620/L-100 computer. A complete deck listing and instruction set of the programmes may be obtained by writing to the authors.

Calorimetric titration procedure

The calorimetric titrations carried out with AEMS are given as an example in Table 2. In each titration the initial volume in the reaction vessel was made up to 80 ml with 0.5 M KNO_3. The heat liberated was calculated as described by Wadsö[2].

MATHEMATICAL TREATMENT AND RESULTS

Symbols

The symbols used in this work are listed below.

Q = total heat liberated by calorimetric titration
Q_{DIL} = heat of dilution of the titrant

Δn_{qrp} = change of the number of moles of $M_qL_rH_p$ between two titration points

Δn_{OH} = change in the number of moles of free OH^-

Δn_B = number of moles base added as titrant

$\Delta n^T_{LH_p}$ = number of moles LH_p added as titrant

$\Delta H'_{qrp}$ = over-all molar enthalpy of formation of the species $M_qL_rH_p$ according to the general reaction

$$qM + rL + pH \rightleftarrows M_qL_rH_p \tag{1}$$

$$\text{with} \quad \begin{aligned} q &= 0 \text{ to } q_{max} \\ r &= 1 \text{ to } r_{max} \\ p &= 0 \text{ to } p_{max} \end{aligned}$$

$\Delta H'_{01p}$ = total molar enthalpy of protonation of L according to $L + pH \rightleftarrows LH_p$

ΔH_w = molar enthalpy of formation of H_2O, from H^+ and OH^-

$\Delta G'_{qrp}, \Delta S'_{qrp}$ = free energy and entropy change of the general reaction (1).

TABLE 2

CONCENTRATION CONDITIONS USED FOR AEMS

Titration No.	C_H	C_L	C_M	*Titrant*
1		0.0863		HNO_3 0.9848 M
2	0.0800	0.0703		$AgNO_3$ 0.5000 M
3	0.0562	0.0526	0.0263	KOH 1.0001 M
4	0.0562	0.0526	0.0125	KOH 1.0001 M
5	0.0639	0.0526	0.0788	KOH 1.0001 M

Calorimetric study

The enthalpy and entropy changes accompanying the protonation of the ligand and the complex formation were determined with the aid of a computer programme KALO, based on the Variable Metric Method for minimization of Davidon[3]. This programme solves the $\Delta H'_{qrp}$ values from eqn (2)

$$-(Q - Q_{DIL}) = \sum_{qrp} \Delta n_{qrp} \Delta H'_{qrp} - \Delta n_{OH} \Delta H_w + \alpha \Delta n_B \Delta H_w + \beta \Delta n^T_{LH_p} \Delta H'_{01p} \tag{2}$$

The coefficient α is equal to 1 for titrations with a base as titrant, otherwise zero, whereas the coefficient β is always zero except when titrating with the ligand LH_p. In this case $\beta = -1$. ΔH_w was taken to be -13.34 kcal mol^{-1} according to Vanderzee and Swanson[4], Hale et al.[5] and our experiments.

As can be seen from eqn (2), the concentration of all species in solution must be calculated for each titration point. This is done using the known β_{qrp} values, the total metal ion concentration C_M, the total ligand concentration C_L

and the analytical hydrogen ion concentration C_H, with a computer programme EQUIL[6].

The entropy changes were calculated from eqn (3)

$$\Delta G'_{qrp} = \Delta H'_{qrp} - T\Delta S'_{qrp} \tag{3}$$

The protonation enthalpies of the ligands may be obtained by titrating the protonated amine with a strong base or the amine itself with a strong acid. We used the latter procedure because the heat evolved was larger. The obtained results are given in Table 3. Calculated standard deviations are given between parenthesis.

TABLE 3

CALORIMETRIC RESULTS FOR THE PROTONATION OF THE LIGANDS

Ligand	$-\Delta G$ *(kcal mol^{-1})*	$-\Delta H$ *(kcal mol^{-1})*	ΔS *(cal mol^{-1} K^{-1})*
HAS	12.792 (1)	12.66 (2)	0.44 (5)
AEMS	12.917 (1)	12.91 (2)	0.02 (5)
AEES	12.878 (1)	12.88 (1)	−0.01 (2)
AEPS	12.894 (1)	12.80 (2)	0.33 (5)
AEBS	12.740 (1)	12.39 (1)	1.18 (1)
APMS	13.770 (1)	13.38 (1)	1.31 (2)
DMAMS	12.290 (1)	9.20 (1)	10.38 (5)
DEAMS	13.040 (1)	10.07 (5)	10.0 (1)
DPAMS	13.462 (2)	10.49 (1)	9.96 (5)

In acid medium only the fully protonated complexes are formed[1], and the corresponding enthalpy changes may be obtained by titrating the metal ion with the protonated ligand or vice versa. For practical reasons we used the latter procedure as can be seen from titration nr. 2 in Table 2.

The number of complexes formed in neutral and alkaline medium is much larger, and their distribution coefficient α, given by eqn (4), depends not only on the ratio C_M/C_L but also on the pH of the solution

$$\alpha_{qrp} = \frac{q\beta_{qrp}(M)^q(L)^r(H)^p}{C_M} \tag{4}$$

We therefore titrated the complexes formed in acid medium at different C_M/C_L ratios with KOH as can be seen from titrations 3–5 in Table 2.

The over-all thermodynamic values, obtained with the minimization procedure were rearranged so as to give the more realistic values corresponding to the reactions given in Table 4. The ΔH value of the $(AgL)^+$ complex could not be determined because its distribution coefficient α did not exceed a maximum value of 5%. For DPAMS only the thermodynamic values of the protonated species could be determined, because of the poor solubility of the ligand in alkaline medium.

TABLE 4

CALORIMETRIC RESULTS FOR THE COMPLEXATION OF THE LIGANDS WITH Ag(I)

	HAS	*AEMS*	*AEES*	*AEPS*	*AEBS*	*APMS*	*DMAMS*	*DEAMS*	*DPAMS*
$Ag^+ + LH^+ \rightleftarrows (AgLH)^{2+}$									
$-\Delta G_{111}$	3.48 (1)	3.60 (1)	4.09 (1)	4.02 (1)	4.57 (1)	4.54 (1)	3.44 (1)	3.53 (1)	3.56 (1)
$-\Delta H_{111}$	6.72 (5)	6.52 (5)	7.42 (2)	7.5 (1)	8.38 (1)	7.55 (5)	6.31 (1)	6.52 (5)	7.05 (1)
ΔS_{111}	−10.9 (1)	−9.8 (2)	−11.2 (1)	−11.7 (4)	−12.77 (5)	−10.1 (2)	−9.64 (5)	−10.1 (2)	−11.70 (5)
$Ag^+ + 2\,LH^+ \rightleftarrows (Ag(LH)_2)^{3+}$									
$-\Delta G_{122}$	5.60 (1)	5.54 (3)	6.35 (1)	6.29 (1)	6.80 (1)	7.64 (1)	5.24 (1)	5.43 (1)	6.00 (4)
$-\Delta H_{122}$	11.10 (5)	13.3 (1)	13.9 (1)	14.1 (1)	14.67 (1)	14.1 (1)	12.51 (2)	12.8 (1)	10.56 (5)
ΔS_{122}	−18.4 (3)	−26.1 (5)	−25.5 (4)	−26.2 (4)	−26.41 (5)	−21.8 (3)	−24.4 (1)	−24.8 (4)	−15.3 (3)
$Ag^+ + LH^+ + L \rightleftarrows (Ag(LH)L)^{2+}$									
$-\Delta G_{121}$	10.28 (1)	10.32 (1)	11.04 (1)	11.02 (1)	11.48 (1)	9.73 (1)	9.11 (2)	9.55 (1)	
$-\Delta H_{121}$	16.8 (1)	17.6 (2)	18.4 (1)	18.6 (1)	17.9 (1)	16.6 (2)	15.8 (1)	13.8 (1)	
ΔS_{121}	−21.7 (3)	−24.5 (6)	−24.5 (3)	−25.5 (5)	−21.7 (3)	−23.1 (7)	−22.4 (5)	−14.3 (3)	
$Ag^+ + 2\,L \rightleftarrows (AgL_2)^+$									
$-\Delta G_{120}$	12.56 (1)	12.67 (1)	13.17 (1)	13.24 (1)	13.63 (1)	10.67 (1)	11.49 (1)	11.82 (1)	
$-\Delta H_{120}$	19.12 (5)	19.6 (1)	20.3 (2)	20.2 (1)	19.70 (5)	17.4 (2)	16.6 (1)	15.23 (2)	
ΔS_{120}	−22.0 (3)	−23.1 (3)	−23.8 (5)	−23.4 (1)	−20.4 (2)	−22.6 (6)	−17.3 (4)	−11.5 (1)	
$2\,Ag^+ + 1\,L \rightleftarrows (Ag_2L_2)^{2+}$									
$-\Delta G_{220}$	17.49 (6)	17.75 (5)	18.63 (5)	18.53 (6)	19.33 (4)	18.68 (2)	15.52 (8)	15.3 (1)	
$-\Delta H_{220}$	28.2 (1)	29.3 (2)	30.4 (1)	31.1 (1)	31.3 (1)	29.6 (1)	21.6 (3)	15.37 (5)	
ΔS_{220}	−35.9 (5)	−38.8 (7)	−39.5 (4)	−42.3 (6)	−40.3 (5)	−36.8 (5)	−20 (1)	−0.2 (5)	
$2\,Ag^+ + L \rightleftarrows (Ag_2L)^{2+}$									
$-\Delta H_{210}$	9.62 (4)	9.36 (7)	10.12 (4)	10.10 (4)	10.74 (2)	9.83 (3)	8.1 (1)	8.41 (4)	
$-\Delta H_{210}$	16.0 (1)	14.85 (5)	17.2 (1)	17.4 (1)	16.6 (1)	14.5 (4)	14.8 (9)	8.34 (5)	
Δs_{210}	−21.4 (6)	−18.4 (4)	−23.7 (5)	−24.6 (6)	−19.6 (4)	−16 (1)	−22 (3)	0.2 (2)	

($-\Delta G$ and $-\Delta H$ in kcal mol^{-1}, ΔS in cal mol^{-1} K^{-1}. Calculated standard deviations between parenthesis.)

DISCUSSION

From Table 3 it can be seen that the protonation enthalpy for the primary amines is more exothermic than for the tertiary amines. As is well-known, this effect must be ascribed to the difference in hydration between the protonated primary and tertiary amines. Hydration occurs via the hydrogen atoms of the protonated amines and as a consequence two more watermolecules are bond on a protonated primary amine. This is confirmed by the larger entropy gain of the tertiary amines (10 e.u.) versus that of the primary amines (0 e.u.). The protonation enthalpy of APMS is more exothermic than that of AEMS and is due to the larger distance of the electron-withdrawing thioether group. The increasing $-\Delta G$ and $-\Delta H$ values among the tertiary amines show that increasing basicity is due to an increasing inductive effect of the substituents.

As stated before[1], in acid medium only the complexes $(Ag(LH))^{2+}$ and $(Ag(LH)_2)^{3+}$ are formed and complexation occurs via the "soft" sulfur atom. The thermodynamic data in Table 4 show that the Ag–S bond of these species is enthalpy-stabilized and that the entropy change strongly counteracts the complex formation. This behaviour and the fact that $-\Delta H_{122}$ is about twice as large as $-\Delta H_{111}$ are typical for soft–soft interactions[7].

The enthalpy changes are more exothermic and the entropy changes are more unfavourable than those of the Ag(I)–amine complexes[8,9]. The obtained results may best be compared with those of the Ag(I)-complexes of $S(CH_2CH_2OH)_2$, investigated by Widmer[10]. For the Ag(I) complexes of the latter ligand the following thermodynamic values were found: $-\Delta G_{11} = 4.9$, $-\Delta H_{11} = 8.0$, $\Delta S_{11} = -10.1$ and $-\Delta G_{12} = 8.2$, $-\Delta H_{12} = 14.8$, $\Delta S_{12} = -20.6$. HAS differs from this ligand by one OH group being replaced by an amino group. Comparing these results with those of HAS, it is seen that the latter ligand forms less stable complexes in acid medium. This is due to a less favourable enthalpy change and can be explained by the electron-withdrawing $CH_2CH_2NH_3^+$ group. From comparison of AEBS with AEMS, it can be seen that the introduction of electron-donating groups such as tert.-butyl tends to strengthen the Ag–S bond. A greater distance of the ammonium group as in APMS has the same effect. As stated before[11], it can be concluded that the Ag–S bond is mainly a σ-bond.

In an earlier paper[1], evidence was found for chelation through N and S for the species $(AgL)^+$ and $(AgL_2)^+$, formed in alkaline medium. An additional support for the formation of chelates is found in the thermodynamic data of these species. Whereas the entropy changes ΔS_{120} and ΔS_{122} for the deprotonated and protonated species are nearly the same, the larger value of $-\Delta G_{120}$ compared with $-\Delta G_{122}$ is due to a much more exothermic enthalpy change, which can only be explained by chelation through S and N. Comparing the thermodynamic values of the Ag complexes of $S(CH_2CH_2OH)_2$, mentioned above, with those of HAS in alkaline medium, where the amino group is no longer protonated, it is seen that the latter ligand now forms more stable complexes. This again is an indication for chelation.

The enthalpy change for the $(AgL_2)^+$ compound of APMS is about 2.2 kcal mol^{-1} less favourable than that of AEMS, which confirms our previous conclusions that six-membered Ag(I) chelates are less stable than five-membered ones. About the same difference is found by Widmer[10] between the »$AgL_2)^+$ chelates of $(-CH_2SCH_2CH_2OH)_2$ and of $H_2C(CH_2SCH_2CH_2OH)_2$. For the Ag(I)–diamine complexes, however, the reverse trend in stability is found[12].

The major species in alkaline medium is $(Ag_2L_2)^{2+}$ and its structure may be compared with the ten-membered ring compound proposed by Schwarzenbach for the Ag(I)–ethyleendiamine system. This complex is characterized by very favourable enthalpy changes and unfavourable entropy changes.

N-substituted ligands show a marked decrease in stability and enthalpy change for the $(Ag_2L_2)^{2+}$ and $(AgL_2)^+$ complexes. The same effect has been established with the silver–amine complexes[13]. An increasing size of the substituents results in a decrease of the heat of reaction due to steric repulsions and the probable formation of less strong Ag–N bonds. On the other hand, the increase of steric crowding favours the desolvation process, so that the reaction-entropy becomes more positive with increasing size of the substituents. This term contributes to the stabilization of the complex, but that cannot compensate the decreasing enthalpic contribution. The thermodynamic values of the $(Ag(LH)L)^{2+}$ species are between those of the $(AgL_2)^+$ and $(Ag(LH)_2)^{3+}$ complexes. It seems, therefore, likely to suppose that the protonated ligand is bound only through the sulfur atom whereas the deprotonated ligand is chelated through N and S.

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