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Thermodynamics of complex formation of Ag(I). Part 9. Investigations on Ag(I)–thiourea–thioacetamide–halide systems in aqueous solution [1]

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Abstract

Mononuclear complex formation in the systems Ag(I)–thiourea–thioacetamide–halide (Cl^-, Br^-, I^-) has been investigated in aqueous solution at constant ionic strength, $\mu = 1$ for KNO_3, and different temperatures.

Predominance diagrams for two-ligand .Ag(I)–thiourea–thioacetamide–halide and three-ligand Ag(I)–thiourea–thioacetamide–halide systems are shown at 25°C.

The suitability of the exponential model $Y = A + B\exp(-CX)$ for describing free energy relationships between the substratum-to-ligand mutual chemical affinities Y and the overall thermodynamic stabilities X of the reacting substrata is stressed.

Compensative enthalpy–entropy relationships have been found both in the overall and the stepwise complex formation.

It is confirmed that favourable enthalpy and unfavourable entropy changes do not necessarily follow soft–soft interactions in aqueous solution.

In the formation of monocoordinate AgL, thiourea and thioacetamide are enthalpically and entropically sharply discriminated in spite of the ligands having the same donor atom.

LIST OF SYMBOLS

L, W, Z	ligand
Tu	thiourea
Ta	thioacetamide
$[X]_{free}$	solvated X molarity
$[X]_{tot}$	total X molarity

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[1] Dedicated to Professor V. Gutmann on the occasion of his 70th birthday.

Sub	Ag(I) complex substratum
β	stability constant for the overall complexing reaction $Ag(I) + iL + jW + mZ = AgL_iW_jZ_m$ ($mol^{-n}\ dm^{3n}$ ($n = i + j + k$))
K	stability constant for the stepwise complexing reaction $Sub + L = Sub\text{–}L$ ($mol^{-1}\ dm^3$)
ΔG, ΔH, ΔS	free energy, enthalpy and entropy change for the K overall complexing reaction ($kJ\ mol^{-1}$, $kJ\ mol^{-1}$, and $J\ mol^{-1}\ K^{-1}$)
$\Delta \bar{G}$, $\Delta \bar{H}$, $\Delta \bar{S}$	free energy, enthalpy and entropy change for the stepwise complexing reaction ($kJ\ mol^{-1}$, $kJ\ mol^{-1}$, and $J\ mol^{-1}\ K^{-1}$)

In some cases, charges, are omitted for simplicity.

INTRODUCTION

The influence of the chemical environment of the central ion on coordination and displacement reactions can be investigated by studying mixed-ligand complex formation.

Our research group has long been concerned with Ag(I) complex formation in systems containing three different ligands. The systems investigated so far are Ag(I)–thiourea–thiosulphate–thiocyanate in aqueous [1] and in aqueous dioxane solutions [2]; Ag(I)–thiourea–thiosulphate–halide (chloride, bromide, iodide) in aqueous solution [3]; Ag(I)–thiourea–thiocyanate–halide (chloride, bromide, iodide) in aqueous solution [4]; and Ag(I)–thiosulphate–thiocyanate–ammonia in aqueous solution [5].

A strongly coordinating ligand (thiourea and/or thiosulphate ion) is always present in the systems to avoid the formation of precipitate; therefore, all the investigated equilibria refer to homogeneous phase reactions.

Both thiosulphate and thiocyanate are S-donor ligands towards Ag(I) and the changes induced by substituting one with the other are probably reflected (or partially reflected) in the changes of the ionic charges of the resulting complexes.

However, on substituting thiourea with ammonia in the coordination sphere of a central ion, the nature of the donor atom changes substantially.

The results of studies on complex formation in Ag(I)–thiourea–thioacetamide–halide (Cl^-, Br^-, I^-) systems are discussed here. A comparison between these systems and the previously investigated Ag(I)–thiourea–thiocyanate–halide and Ag(I)–thiourea–thiosulphate–halide systems is made. Thioacetamide is an S-donor as $S_2O_3^{2-}$ or SCN^-, but is a zero-charged ligand. It is differentiated from thiourea by the presence of a hydrophobic $-CH_3$ group instead of a hydrophillic $-NH_2$ group. Complexing reactions with thioacetamide must, therefore, comprise a different role for the solvent than in complexing reactions with the other investigated ligands.

EXPERIMENTAL

Chemicals

Potassium salts were used for the halide solutions. $AgNO_3$ was the source for the Ag(I) solutions. Thiourea and thioacetamide solutions were prepared by direct weighing of material recrystalized from acetone, washed with ether and vacuum dried.

Measurements

The measurements were made by potentiometry using a silver wire as test electrode connected to a saturated calomel electrode (SCE) as reference. The apparatus was an Amel model 334 potentiometer. Titrations were performed in a thermostated cell at constant ionic strength $\mu = 1$ for KNO_3.

Procedure

Solutions containing $AgNO_3$, thiourea, thioacetamide (all three in constant amounts) and KNO_3 up to $\mu = 0.5 \sum C_i Z_i^2 = 1$ (Z is ionic charge, C is molarity) were titrated against KL (where L is Cl^-, Br^-, I^-) solution with $\mu = 1$ for KL + KNO_3.

In order to have stable, colourless Ag(I)–thiourea–thioacetamide solutions they were prepared as previously described [3, 4].

Scheme 1 indicates the investigated concentration ranges:

$[AgNO_3]_{tot}$	2×10^{-7}	to	1×10^{-6} M	(five different concentrations)
$[Thiourea]_{tot}$	1×10^{-4}	to	8×10^{-4} M	(six different concentrations)
$[Thioacetamide]_{tot}$	0	to	7×10^{-3} M	(ten different concentrations)
$[KCl]_{tot}$	0	to	0.285 M	(six different concentrations)
$[KBr]_{tot}$	0	to	0.285 M	(six different concentrations)
$[KI]_{tot}$	4×10^{-6}	to	2×10^{-5} M	(six different concentrations)

Scheme 1. Concentration range.

About 1500 titrations (300 titrations at each temperature) were performed for 7500–8000 experimental points.

The measuring cell can be represented as shown in Scheme 2. Calculations were made as previously reported [1–3].

Ag	$[AgNO_3]_{tot}$	= constant	KNO_3	SCE
	$[Tu]_{tot}$	= constant	sat.	
	$[Ta]_{tot}$	= constant	salt	
	$[KNO_3]$	= constant to $\mu = 1$	bridge	
	[KL]	= variable		

Scheme 2. The measuring cell.

TABLE 1

Log β_n ($mol^{-n}\,dm^{3n}$) for the overall complex formation Ag(I)–thiourea–thioacetamide–halide (Cl^-, Br^-, I^-) in aqueous solution and ionic strength $\mu = 1$ for KNO_3 at different temperatures

Formula	Halide	0°C	10°C	15°C	20°C	25°C	30°C	35°C
$AgTa^+$	Cl^-	8.45 ± 0.1	–	9.0 ± 0.1	8.59 ± 0.1	8.53 ± 0.1	–	8.99 ± 0.1
	Br	8.76 ± 0.2	8.36 ± 0.2	–	8.81 ± 0.2	8.60 ± 0.3	9.11 ± 0.3	–
	I^-	9.83 ± 0.2	8.14 ± 0.1	–	7.02 ± 0.3	7.16 ± 0.2	–	–
$AgTu^+$	Cl^-	7.73 ± 0.1	–	7.97 ± 0.1	7.20 ± 0.1	7.83 ± 0.1	–	7.64 ± 0.1
	Br^-	8.55 ± 0.1	8.00 ± 0.2	–	8.13 ± 0.1	7.94 ± 0.1	8.62 ± 0.1	–
	I^-	8.86 ± 0.1	6.33 ± 0.2	–	6.23 ± 0.1	6.41 ± 0.1	–	–
$AgTu_2^+$	Cl^-	11.85 ± 0.05	–	10.81 ± 0.3	10.97 ± 0.6	–	–	–
	Br^-	12.37 ± 0.1	18.85 ± 0.2	–	11.45 ± 0.3	–	–	–
	I^-	–	–	–	–	–	–	–
$AgTuTa^+$	Cl^-	11.22 ± 0.5	–	–	10.95 ± 0.1	11.80 ± 0.2	–	11.72 ± 0.3
	Br^-	11.59 ± 0.3	12.45 ± 0.2	–	11.45 ± 0.5	11.63 ± 0.4	12.07 ± 0.4	–
	I^-	10.07 ± 0.8	9.69 ± 0.4	–	9.41 ± 0.1	9.12 ± 0.3	–	–
AgCl	Cl^-	4.99 ± 0.1	–	4.95 ± 0.3	4.03 ± 0.6	4.97 ± 0.2	–	5.13 ± 0.1
AgClTu	Cl^-	8.61 ± 0.4	–	8.33 ± 0.5	8.31 ± 0.3	8.48 ± 0.2	–	8.25 ± 0.3
AgClTa	Cl^-	8.38 ± 0.2	–	–	8.73 ± 0.1	9.46 ± 0.1	–	9.48 ± 0.3
AgClTuTa	Cl^-	12.24 ± 0.6	–	–	–	–	–	–
$AgClTu_2$	Cl^-	12.33 ± 0.1	–	–	–	–	–	–
$AgCl_2^-$	Cl^-	5.69 ± 0.1	–	–	5.77 ± 0.3	5.77 ± 0.1	–	–
$AgCl_2Ta^-$	Cl^-	8.79 ± 0.3	–	–	8.86 ± 0.3	–	–	–
$AgCl_2Tu^-$	Cl^-	9.32 ± 0.1	–	–	–	–	–	–
AgBr	Br^-	6.89 ± 0	6.05 ± 0.1	–	6.29 ± 0.1	5.95 ± 0	6.02 ± 0.1	–
AgBrTu	Br^-	9.93 ± 0.2	9.81 ± 0.1	–	9.13 ± 0.1	9.15 ± 0.1	9.45 ± 0.3	–
AgBrTa	Br^-	10.01 ± 0.1	9.62 ± 0.5	–	9.09 ± 0.4	8.45 ± 0.6	9.48 ± 0.3	–
$AgBrTu_2$	Br^-	13.41 ± 0.1	13.24 ± 0.1	–	12.59 ± 0.1	–	–	–
AgBrTuTa	Br^-	13.14 ± 0.5	13.22 ± 0.4	–	12.66 ± 0.3	12.14 ± 1	–	–
$AgBr_2^-$	Br^-	8.46 ± 0.1	7.62 ± 0.1	–	7.59 ± 0.1	7.51 ± 0.1	7.32 ± 0.1	–
$AgBr_2Ta^-$	Br^-	–	12.52 ± 0.1	–	10.41 ± 0.2	10.16 ± 0.4	10.25 ± 0.2	–
$AgBr_2Tu^-$	Br^-	11.46 ± 0.1	10.9 ± 0.1	–	10.83 ± 0.3	10.16 ± 0.5	10.27 ± 0.1	–
AgI	I^-	9.85 ± 0.1	9.13 ± 0.2	–	8.58 ± 0.1	8.56 ± 0.1	–	–
AgITu	I^-	12.99 ± 0.1	12.12 ± 0.3	–	–	11.70 ± 0.6	–	–
AgITa	I^-	13.47 ± 0.3	12.24 ± 0.9	–	10.91 ± 0.1	12.98 ± 0.2	–	–
AgITuTa	I^-	–	15.67 ± 1.0	–	–	15.22 ± 0.7	–	–
AgI_2^-	I^-	13.22 ± 0.1	13.91 ± 0.1	–	13.36 ± 0.1	13.14 ± 0.1	–	–
AgI_2Ta^-	I^-	16.28 ± 1.0	17.45 ± 0.4	–	16.26 ± 0.2	16.05 ± 0.6	–	–

RESULTS AND DISCUSSION

Table 1 lists the identified complexes in the various systems (indicated in column S) and their cumulative stability constants at different temperatures and constant ionic strength, $\mu = 1$ for KNO_3.

The free energy, enthalpy and entropy changes at 25°C listed in Table 2 were deduced from the linear dependence of ΔG on temperature, using data from both Table 1 and from previous papers on the Ag(I)–thiourea–halide complexes [1, 3, 4]. As more ΔG values for the same complex at the same temperature became available, the mean value was introduced in the calculation, e.g. for the formation of $AgTa^+$ at $T = 0$°C, 47.13 kJ mol^{-1} was used as ΔG which is the mean value of the set of data reported in Table 1 at $\theta = 0$°C.

The thermodynamic parameters for single-ligand coordination reactions, Sub + L = Sub–L, are reported in Table 3.

TABLE 2

Most probable log β_n (mol^{-n} dm^{3n}), free energy, enthalpy and entropy changes (kJ mol^{-1}, kJ mol^{-1}, and kJ mol^{-1} K^{-1}, respectively) for the overall complex formation Ag(I)–thiourea–thioacetamide–halide (Cl^-, Br^-, I^-) in aqueous solution and ionic strength $\mu = 1$ for KNO_3 at 25°C

Formula	log β	$-\Delta G$	ΔH	ΔS	I [a]
$AgTa^+$	8.56	48.84	2 ± 10	171 ± 38	3
$AgTu^+$	7.59	43.34	−65 ± 11	−72 ± 39	3
$AgTu_2^+$	10.35	59.07	−93 ± 4	−114 ± 14	3
$AgTuTa^+$	11.25	64.22	52 ± 24	390 ± 80	3
AgCl	4.44	25.34	−26 ± 9	−4 ± 30	3
AgClTu	8.33	47.55	−42 ± 3	17 ± 9	3
AgClTa	9.19	52.46	54 ± 19	358 ± 64	–
$AgCl_2^-$	5.21	29.73	−21 ± 9	31 ± 32	3
$AgCl_2Tu^-$	8.57	48.92	−75 ± 6	−89 ± 20	3
AgBr	6.34	36.19	−32 ± 25	14 ± 83	3
AgBrTu	9.36	53.43	−66 ± 23	42 ± 78	3
AgBrTa	8.93	50.99	−60 ± 25	−32 ± 87	3
$AgBrTu_2$	12.53	71.5	−71 ± 7	−3 ± 25	3
AgBrTuTa	12.31	70.25	−67 ± 22	11 ± 76	–
$AgBr_2^-$	7.44	42.48	−44 ± 9	−6 ± 32	3
$AgBr_2Ta^-$	10.39	59.3	−193 ± 64	−450 ± 218	–
$AgBr_2Tu^-$	10.39	59.3	−69 ± 8	−34 ± 29	3
AgI	9.02	51.49	−22 ± 40	98 ± 139	3
AgITu	11.82	67.48	−53 ± 8	49 ± 30	3
AgITa	11.91	67.99	−69 ± 101	−4 ± 352	–
AgI_2^-	12.64	72.13	−57 ± 16	51 ± 56	3
AgI_2Ta^-	16.28	92.9	−34 ± 59	199 ± 209	–

[a] Number of consecutive points used for smoothing the original data before evaluating the figures of the table.

TABLE 3

Most probable log K (mol^{-1} dm^3), free energy, enthalpy and entropy changes (kJ mol^{-1}, kJ mol^{-1}, and J mol^{-1} K^{-1}, respectively) for the stepwise complex formation Ag(I)–theourea–thioacetamide–halide (Cl^-, Br^-, I^-) in aqueous solution at 25°C and ionic strength $\mu = 1$ for KNO_3

Reaction	log K	$-\Delta G$	ΔH	ΔS
Entering group, Tu				
$Ag(I) + Tu = AgTu^+$	7.59	43.34	−63	−72
Monocoordinated substrata				
$AgTu^+ + Tu = AgTu_2^+$	2.76	16.36	−28	−42
$AgTa^+ + Tu = AgTuTa^+$	2.69	15.38	49	219
$AgCl + Tu = AgClTu$	3.89	22.21	−16	21
$AgBr + Tu = AgBrTu$	3.02	17.24	−34	−56
$AgI + Tu = AgITu$	2.8	15.99	−31	−49
Bicoordinated substrata				
$AgCl_2^- + Tu = AgCl_2Tu^-$	3.36	19.19	−55	−120
$AgBr_2^- + Tu = AgBr_2Tu^-$	2.95	16.82	−25	−28
$AgBrTu + Tu = AgBrTu_2$	3.17	18.07	−5	39
$AgBrTa + Tu = AgBrTaTu$	3.92	19.25	−7	43
Entering group, Ta				
$Ag(I) + Ta = AgTa^+$	8.56	48.84	2	171
Monocoordinated substrata				
$AgTu^+ + Ta = AgTuTa^+$	3.66	20.88	117	462
$AgCl + Ta = AgClTa$	4.75	27.12	80	362
$AgBr + Ta = AgBrTa$	2.59	14.80	−28	−46
$AgI + Ta = AgITa$	2.89	16.50	−47	−102
Bicoordinated substrata				
$AgBr_2^- + Ta = AgBr_2Tu^-$	2.95	16.82	−149	−444
$AgBrTu + Ta = AgBrTuTa$	2.95	16.82	−1	53
$AgI_2^- + Ta = AgI_2Ta^-$	3.64	20.77	23	148
Entering group, Cl^-				
$Ag(I) + Cl^- = AgCl$	4.44	25.34	−26	−4
Monocoordinated substrata				
$AgTu^+ + Cl^- = AgClTu$	0.74	4.21	23	89
$AgTa^+ + Cl^- = AgClTa$	0.63	3.62	52	187
$AgCl + Cl^- = AgCl_2^-$	0.77	4.39	5	35
Bicoordinated substrata				
$AgClTu + Cl^- = AgCl_2Tu^-$	0.24	1.37	−33	−106
Entering group, Br^-				
$Ag(I) + Br^- = AgBr$	6.34	36.19	−32	14
Monocoordinated substrata				
$AgTu^+ + Br^- = AgBrTu$	1.77	10.10	−1	30
$AgTa^+ + Br^- = AgBrTa$	0.37	2.16	−62	−203
$AgBr + Br^- = AgBr_2^-$	1.17	6.29	−120	−20

TABLE 3 (continued)

Reaction	log K	$-\Delta G$	ΔH	ΔS
Bicoordinated substrata				
$AgTuTa^- + Br^- = AgTuTaBr$	1.06	6.03	−119	−379
$AgTu_2^+ + Br^- = AgBrTu_2$	2.18	12.43	22	111
$AgBrTu + Br^- = AgBr_2Tu^-$	1.03	5.87	−3	8
$AgBrTa + Br^- = AgBr_2Ta^-$	1.46	8.31	−133	−418
Entering group, I^-				
$Ag(I) + I^- = AgI$	9.02	51.49	−22	98
Monocoordinated substrata				
$AgTu^+ + I^- = AgITu$	4.23	24.14	12	121
$AgTa^+ + I^- = AgITa$	3.35	19.15	−71	−175
$AgI + I^- = AgI_2^-$	3.62	20.64	−35	−47
Bicoordinated substrata				
$AgITa + I^- = AgI_2Ta^-$	4.37	25.42	35	203

Under the experimental conditions employed in the present work, solvated Ag(I) and monocoordinated or bicoordinated Ag(I) substrata bind only one thioacetamide ligand, forming complexes that are up to tricoordinates at most.

Thiourea forms bicoordinates with Ag(I) and AgCl or AgBr substrata. Bicoordinates are also formed by halides reacting with Ag(I).

Mixed two-ligand bi- and tricoordinates (ML_iW_j, $i + j = 2$ or 3) and three-ligand tricoordinates (MLWZ) occur. The most disfavoured tricoordinated three-ligand complex appears to be AgClTuTa, which has been identified at only one temperature (see Table 1), and is not reported among the complexes in Table 2.

Comparisons with the previous data

For most of the complexes in Table 2, thermodynamic data for their formation have already been published by our laboratory using the same experimental conditions (ionic strength, background electrolyte and solvent) as in the present work and total agreement exists for the free energy data. The same is true, for the enthalpy changes for the formation of $AgTu^+$, $AgTu_2^+$, AgTuCl, AgBr, AgBrTu, $AgBrTu_2$ and AgITu. Partial agreement is found for the halide complexes AgCl, $AgCl_2^-$ and AgI. For the formation of AgCl, $\Delta H = -26$ kJ mol^{-1} is given here but previously [4] -44 kJ mol^{-1} was found; for the formation of $AgCl_2$, $\Delta H = -20.5$ kJ mol^{-1} here, against -44 kJ mol^{-1} [4] was found; and finally, for AgI,

$\Delta H = -28\ \mathrm{kJ\ mol^{-1}}$ here and $\Delta H = -38.5\ \mathrm{kJ\ mol^{-1}}$ previously [4]. The entropy change results are similar.

It can be concluded that the free energy data at 25°C in Table 2 can be considered highly reliable because of the close agreement found between present and previous figures; the same is true for the ΔH values for which total concordance is found.

For ΔH and ΔS for the complexive formation of $AgCl_n^{1-n}$ ($n = 1$–2) and AgI, whose concordance with literature data is only partial, the values reported in Table 2 must be considered more reliable than the previous ones because they are deduced with inclusion of the previously published free energy data.

For the complexes not investigated in our laboratory, the enthalpy and entropy changes must be considered with due caution, notwithstanding the high number of measurements.

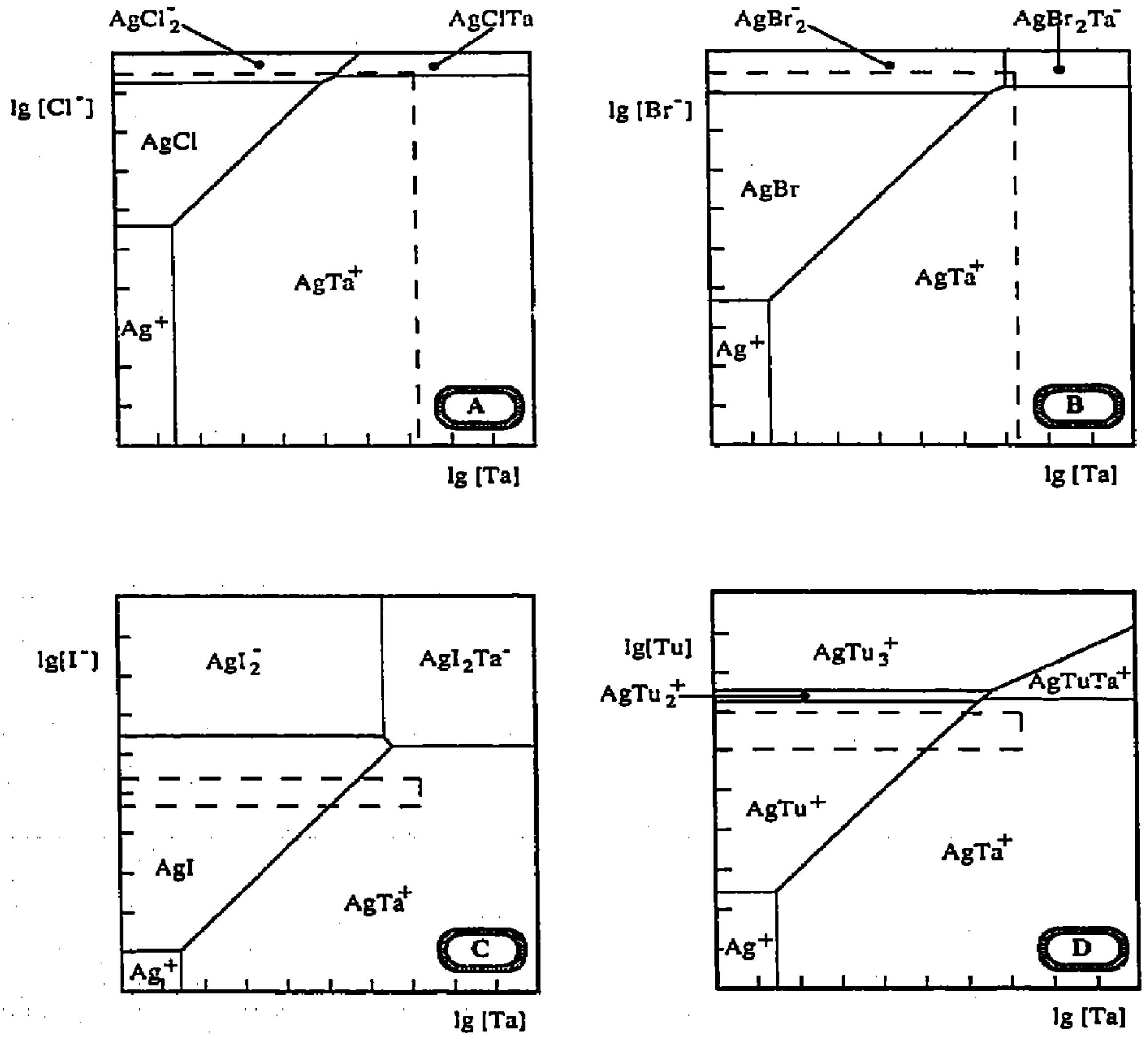


Fig. 1.

Predominance diagrams

The predominance diagrams in two- and three-ligand systems are shown in Figs. 1 and 2 respectively. The diagrams were calculated by means of the configuration reported in the captions of the figures. In Fig. 1, the broken lines delimit the experimentally investigated concentration ranges.

In solution, the simultaneous presence of high concentrations of thioacetamide and halide allows mixed thioacetamide–halide Ag(I) complexes to predominate. AgClTa (Fig. 1A) is formed mainly (i) for chloride coordination to $AgTa^+$ (reaction, $AgTa^+ + Cl^- = AgClTa$) or (ii) for chloride displacement from $AgCl_2^-$ (reaction, $AgCl_2^- + Ta = AgClTa + Cl^-$).

For the formation of $AgBr_2Ta^-$ or AgI_2Ta^- (Fig. 1B and C), the simultaneous coordination of two halide ligands to $AgTa^+$, or thioacetamide coordination to bi-halide Ag(I) complex, prevails (reactions, $AgTa^+ + 2L = AgL_2Ta^-$ or $AgL_2^- + Ta = AgL_2Ta^-$; $L = Br^-$ or I^-).

In the two-ligand system Ag(I)–Tu–Ta, the predominating mixed species $AgTuTa^+$ is formed by thiourea coordination to $AgTa^+$ (reaction,

Fig. 1. Predominance diagrams for the two-ligand systems in aqueous solution at 25°C and ionic strength $\mu = 1$ for KNO_3.

Formula	A Ag(I)–Cl^-–Ta log β	B Ag(I)–Br^-–Ta log β	C Ag(I)–I^-–Ta log β	D Ag(I)–Tu–Ta log β
Ag(I)	0	0	0	0
$AgTa^+$	8.56	8.56	8.56	8.56
AgCl	4.44	–	–	–
AgClTa	9.19	–	–	–
$AgCl_2^-$	5.21	–	–	–
$AgBr^2$	–	6.34	–	–
$AgBr_2^-$	–	7.44	–	–
AgBrTa	–	8.93	–	–
$AgBr_2Ta^-$	–	10.39	–	–
AgI	–	–	9.02	–
AgITa	–	–	11.21	–
AgI_2^-	–	–	12.64	–
AgI_2Ta^-	–	–	12.68	–
$AgTu^+$	–	–	–	7.59
$AgTu_2^+$	–	–	–	10.35
$AgTu_3^+$	–	–	–	12.87
$AgTuTa^+$	–	–	–	11.25

The broken lines delimit the investigated concentration ranges.

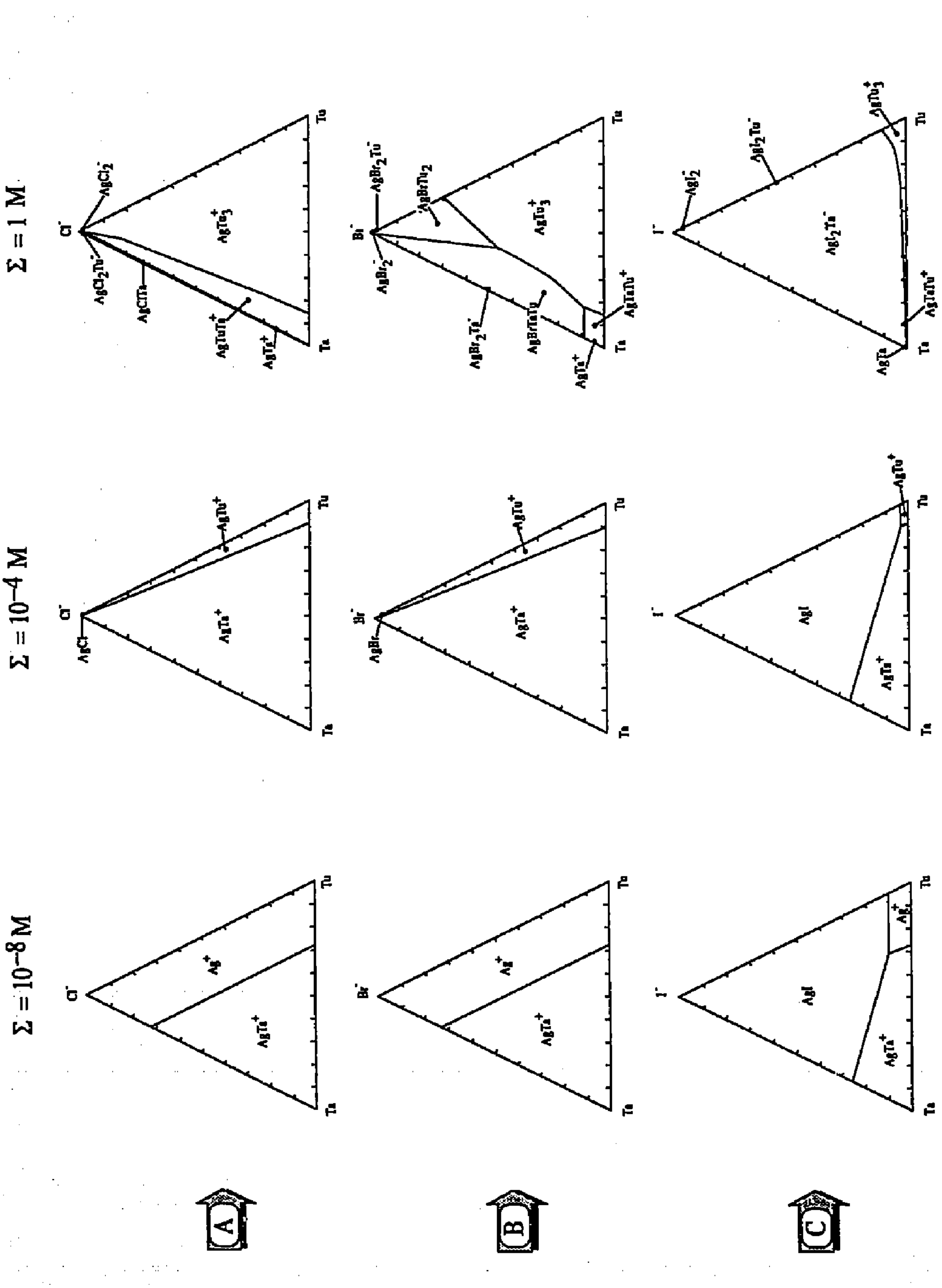

Σ = 10⁻⁸ M
Σ = 10⁻⁴ M
Σ = 1 M
A
B
C
Cl⁻
Br⁻
I⁻
Ta
Tu
Ag⁺
AgTa⁺
AgTu⁺
AgCl
AgBr
AgI
AgCl₂⁻
AgCl₂Tu⁻
AgClTa
AgTuTa⁺
AgTu₃⁺
AgBr₂⁻
AgBr₂Tu⁻
AgBrTu₂
AgBr₂Ta⁻
AgBrTaTu
AgTaTu⁺
AgI₂⁻
AgI₂Tu⁻
AgI₂Ta⁻
AgTa

Fig. 2.

$AgTa^+ + Tu = AgTuTa^+$) or by displacement of two thiourea molecules from $AgTu_3^+$ (reaction, $AgTu_3^+ + Ta = AgTuTa^+ + 2Tu$).

Predominance diagrams for the three-ligand systems Ag(I)–Tu–Ta–L (where L is Cl^-, Br^-, I^-) have been drawn for different $\Sigma [L]_{free} = [Tu]_{free} + [Ta]_{free} + [Z]_{free}$ values (1×10^{-8} M, 1×10^{-4} M and 1 M). As in Fig. 1, the interpretation and critical analysis of the diagrams must take into account (i) the configuration of the complexes and (ii) the possible occurrence of more complexes especially with thioacetamide.

At $\Sigma [L]_{free}$ values (1×10^{-4} M) where the formation of monocoordinates is predominant (see Fig. 1), the areas for the respective complexes are the result of the quantitative relationships among the stability constants.

Fig. 2. Predominance diagrams for the three-ligand systems in aqueous solution at 25°C and $\mu = 1$ for KNO_3 at different $[Tu]_{free} + [Ta]_{free} + [L]_{free}$ constant values.

Formula	A Ag(I)–Tu–Ta–Cl^- log β	B Ag(I)–Tu–Ta–Br^- log β	C Ag(I)–Tu–Ta–I^- log β
Ag(I)	0	0	0
$AgTa^+$	8.56	8.56	8.57
$AgTu^+$	7.59	7.59	7.59
$AgTu_2^+$	10.35	10.35	10.35
$AgTu_3^+$	12.87	12.87	12.87
$AgTuTa^+$	11.25	11.25	11.25
AgCl	4.44	–	–
$AgCl_2^-$	5.21	–	–
AgClTa	9.19	–	–
AgClTu	8.33	–	–
$AgCl_2Tu^-$	8.57	–	–
AgBr	–	6.34	–
AgBrTa	–	8.93	–
AgBrTu	–	9.36	–
	–		
$AgBrTu_2$	–	12.53	–
AgBrTuTa	–	12.31	–
AgBrTa	–	8.93	–
$AgBr_2^-$	–	7.44	–
$AgBr_2Tu^-$	–	10.39	–
$AgBr_2Ta^-$	–	10.39	–
AgI	–	–	9.02
AgITu	–	–	11.82
AgITa	–	–	11.91
AgI_2^-	–	–	12.62
AgI_2Ta^-	–	–	16.28
AgI_2Tu^-	–	–	13.47

At high $\Sigma\,[\mathrm{L}]_{\mathrm{free}}$ values (1 M), single-ligand and mixed-ligand complexes with different complexive coordination levels occur. The surface extensions also depend on this factor, as well as on the stability constants. Whilst at low $\Sigma\,[\mathrm{L}]_{\mathrm{free}}$ values (1×10^{-4} M), where single-ligand complexes predominate, the most important species in the three-ligand systems is the one for which Ag(I) shows the highest affinity ($\mathrm{AgTa^+}$ in the systems Ag(I)–Tu–Ta–$\mathrm{Cl^-}$ and Ag(I)–Tu–Ta–$\mathrm{Br^-}$, AgI in the system Ag(I)–Tu–Ta–$\mathrm{I^-}$), with high $\Sigma\,[\mathrm{L}]_{\mathrm{free}}$ values, $\mathrm{AgTu_3^+}$ (the single-ligand complex with the highest coordination number among the identified complexes) becomes the most important complex. The higher coordination number with respect to thiourea, compared with the other ligands, is responsible for the different predominance of $\mathrm{AgTu_3^+}$ on going from $\Sigma\,[\mathrm{L}]_{\mathrm{free}} = 1 \times 10^{-4}$ to 1 M.

Free energy changes

Free energy changes are sensitive to experimental conditions, such as temperature, composition of the solvent medium, ionic strength, etc. Overall and single-ligand coordination reactions (whose thermodynamic data are reported in Tables 2 and 3 respectively) show different dependences on temperature change (ΔS). As a consequence, the free energy relationships are also temperature dependent, and for some of them (namely, order relationships and stability sequences) the possibility of inversion is easily foreseen. Inversion is clearly associated with the occurrence of one experimentally accessible isoequilibrium condition. When more isoequilibrium points occur, each one of them can be assumed to be a parameter for identifying and probably characterizing subsets in the considered set of reactions [6]. In such cases at least three different order relationships or stability sequences are identified.

The relationships deduced and discussed here refer to experimental conditions indicated in Table 2.

The chemical affinities toward thioacetamide and the other investigated ligands allow Ag(I) mono- and bicoordinated Ag(I) substrata to be classified into two groups: one is formed by the single solvated Ag(I), the other includes simultaneously monocoordinated and bicoordinated substrata (Fig. 3). The substratum-to-ligand affinity distributions do not distinguish between monocoordinates and bicoordinates. The distance (the differences in free energy changes) between the groups is on the whole independent of the incoming ligand.

On the basis of the ΔG values for the reaction series $\mathrm{Ag(I) + L = AgL}$, thioacetamide lies closer to iodide than to the parent thiourea. Moreover, in several cases Ta shows higher affinities towards bicoordinated substrata than $\mathrm{Br^-}$ or $\mathrm{I^-}$ do towards monocoordinates.

The overall free energy changes for the reactions $\mathrm{Ag(I) + L + Z + W = AgLZW}$ can be assumed as the basis for an affinity scale towards

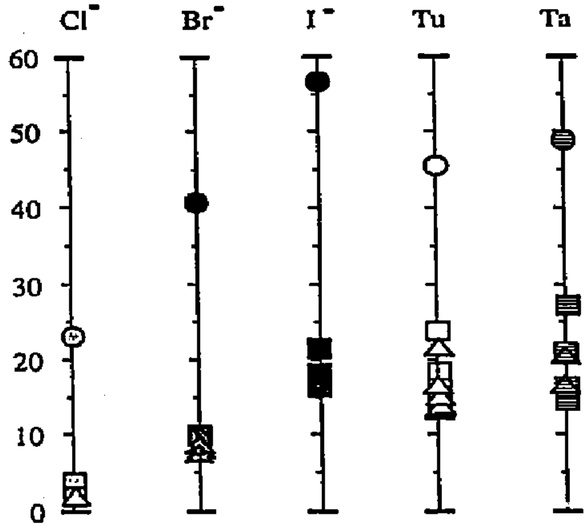


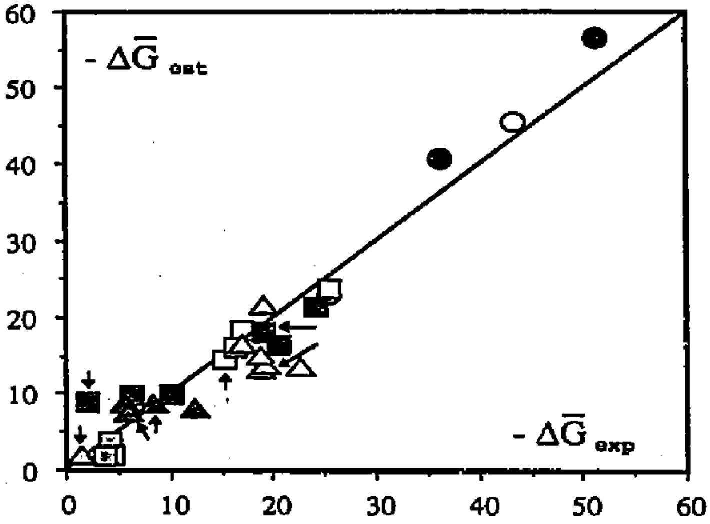
Fig. 3. Free energy pattern (kJ mol^{-1}) for the reactions Sub + L = Sub–L at 25°C and $\mu = 1$ for KNO_3 in aqueous solution. The different lines correspond to different entering ligands: ○, reaction Ag(I) + L = AgL; □, reaction AgW + L = AgWL; △, reaction AgWZ + L = AgWZL.

groups of *n* ligands. In the reactions for the overall formation of bicoordinates with thioacetamide as constant ligand along the series (series of reactions, Ag(I) + Ta + L = AgTaL; L = variable), the experimental stability order is

$$(Br^-, Ta) \leq (Cl^-, Ta) < (Tu, Ta) < (I^-, Ta) \qquad (1)$$

Relationship (1) reflects the affinity order towards single ligands (see Table 2), except the relationship between the pairs (Br^-, Ta) and (Cl^-, Ta). The same occurs in the series of reactions for the cumulative formation of bicoordinates where thioacetamide is variable along the series. For the series of reactions $Ag(I) + Cl^- + L = AgClL$, the affinity sequence towards Ag(I) is $(Cl^-, Cl^-) < (Cl^-, Tu) < (Cl^-, Ta)$. For the series of reactions Ag(I) + Br + L = AgBrL, the affinity sequence toward Ag(I) is $(Br^-, Br^-) < (Br^-, Ta) < (Br^-, Tu)$. For the series of reactions $Ag(I) + I^- + L = AgIL$, the affinity sequence toward Ag(I) is $(I^-, Tu) \leq (I^-, Ta) \leq (I^-, I^-)$. For the series of reactions Ag(I) + Tu + L = AgTuL, the affinity sequence toward Ag(I) is $(Tu, Cl) < (Tu, Br^-) < (Tu, Tu) < (Tu, Ta) < (Tu, I^-)$. It can be concluded that in the case of thioacetamide also, the additive criterium [4, 6] in building up the affinity scale for pairs of ligands from the affinities towards single ligands still works well enough. The only exception is the relationship between the pairs (Br^-, Ta) and (Br^-, Tu) in the reaction series $Ag(I) + Br^- + L = AgBrL$. Of course the additivity must only be applied for qualitative relationships (the affinity sequences).

The substratum-to-ligand chemical affinities depend on the thermodynamic stabilities of the reacting substrata. It has been demonstrated [7, 8] that in the series of reactions between various complex substrata of the same central ion and the same ligand, conditions occur where the affinities towards single entering ligand can be described by means of an exponential model with the free energy change for the overall formation of the reacting substrata as independent variable. (For the series of reactions $\mathrm{Sub}_{(i)} + \mathrm{L} = \mathrm{Sub}_{(i)}\text{–}\mathrm{L}$, $\mathrm{Sub}_{(i)}$ = variable and L = constant, the model is $Y = A + B\exp(-CX)$ with $Y = -\Delta\bar{G}$ for the reaction $\mathrm{Sub}_{(i)} + \mathrm{L} = \mathrm{Sub}_{(i)}\text{–}\mathrm{L}$ and $X = -\Delta G$ for the overall formation of the reacting substrata.) The model describes at times the behaviour of the whole set of substrata (solvated central ion + monocoordinated substrata + bicoordinated substrata), and at times discriminates between monocoordinated and bicoordinated substrata. With fixed experimental conditions and central ion, the parameters A, B and C are characteristic of the incoming ligand.



Meaning of the symbols:

Entering group	Tu	Cl⁻	Br⁻	I⁻
Ag(I)	○	⊙	●	●
Monocoord sub.	□	⊠	■	■
Bicoord sub.	△	△	▲	▲

Fig. 4. Relationship between experimental $\Delta\bar{G}_{\mathrm{exp}}$ (abscissa) and estimated $\Delta\bar{G}_{\mathrm{est}}$ (ordinate) free energy changes (kJ mol^{-1}) for the stepwise coordination reactions Sub + L = Sub–L in Ag(I) complex formation. Experimental conditions: aqueous solution, 25°C, ionic strength $\mu = 1$ for $\mathrm{KNO_3}$. Model: $Y = A + B\exp(-CX)$ where $Y = \Delta\bar{G}_{\mathrm{est}}$ and X = free energy changes for the overall complex formation of the reacting substratum. Values of the parameters A, B, and C, respectively (kJ mol^{-1}) [7] for the different entering groups: Tu, 1.279, 9.613, 0.128; $\mathrm{Cl^-}$, 0.313, 5.20, 0.364; $\mathrm{Br^-}$, 1.561, 8.143, 0.226; $\mathrm{I^-}$, −11.177, 24.689, 0.04. Least-squares estimated linear regression (not drawn in figure): $\Delta\bar{G}_{\mathrm{est}} = -0.771(\pm 1.6) + 0.978(\pm 0.08)\Delta\bar{G}_{\mathrm{exp}}$ (standard deviations in parentheses).

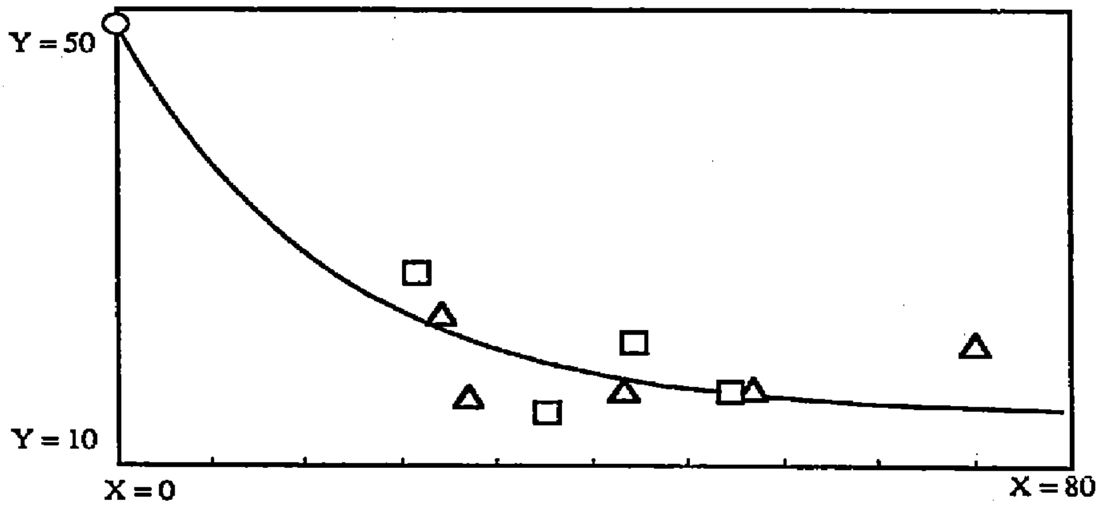


Fig. 5. Non-linear free energy relationship (NLFER) between the substratum-to-ligand affinities ($-\Delta\bar{G}$ for the reaction Sub + L = Sub–L) and the complexive thermodynamic stabilities of the reacting substrata ($-\Delta\bar{G}$ for the overall formation of Sub). Entering group: thioacetamide. Experimental conditions: aqueous solution, 25°C, ionic strength $\mu = 1$ for KNO_3. Model: $Y = A + B\exp(-CX)$ (kJ mol^{-1}). Estimated values for the parameters A, B and C (kJ mol^{-1}) by mean least-squares fitting: $A = 14.46 \pm 3.6$; $B = 34.63 \pm 52$; $C = 0.055 \pm 0.02$. Symbols: ○, Ag(I); □, monocoordinated substrata; △, bicoordinated substrata.

The A, B and C values for some entering ligands have been evaluated with a data set concerning Ag(I) mixed-ligand complex formation [7]. The values, previously and independently obtained from the data presently reported, have been used with the complexive thermodynamic stabilities of substrata given here for calculating the substratum-to-ligand chemical affinities. The close agreement between the point-pattern and the identity relationship ($\Delta G_{est} = \Delta G_{exp}$: the diagonal drawn in the diagram of Fig. 4) demonstrates the quality of the proposed model for describing the substratum-to-ligand affinities[2] on the basis of the thermodynamic stabilities of the reacting substrata. The large free energy range covered, ≈60–70 kJ mol^{-1}, corresponding to 10–14 log K units at 25°C, and the considerable agreement between the estimated and experimental values for complex substrata with thioacetamide among the coordinated ligands (marked with an arrow in Fig. 4) must be stressed. These substrata were not included in calculating the employed A, B and C values.

For the reaction series $Sub_{(i)} + Ta = Sub_{(i)}\text{–}Ta$, asymptotic behaviour is

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[2] In table 2 of ref. [7] the following wrong values are given:
Entering group Br^- $A = -1.516$ kJ mol^{-1} (erratum)
Correct value $A = 1.516$ kJ mol^{-1}
Entering group I^- $C = 0.004$ kJ mol^{-1} (erratum)
Correct value $C = 0.04$ kJ mol^{-1}.

fairly evident. For this entering group the exponential model has also been fitted to the substratum-to-ligand affinities (Fig. 5).

Enthalpy and entropy changes

The complexive coordination reactions are exothermal in nature, with a few exceptions (see Table 2). The ΔH and ΔS values are clearly related to each other in two parallel patterns (Fig. 6). The evident enthalpy–entropy

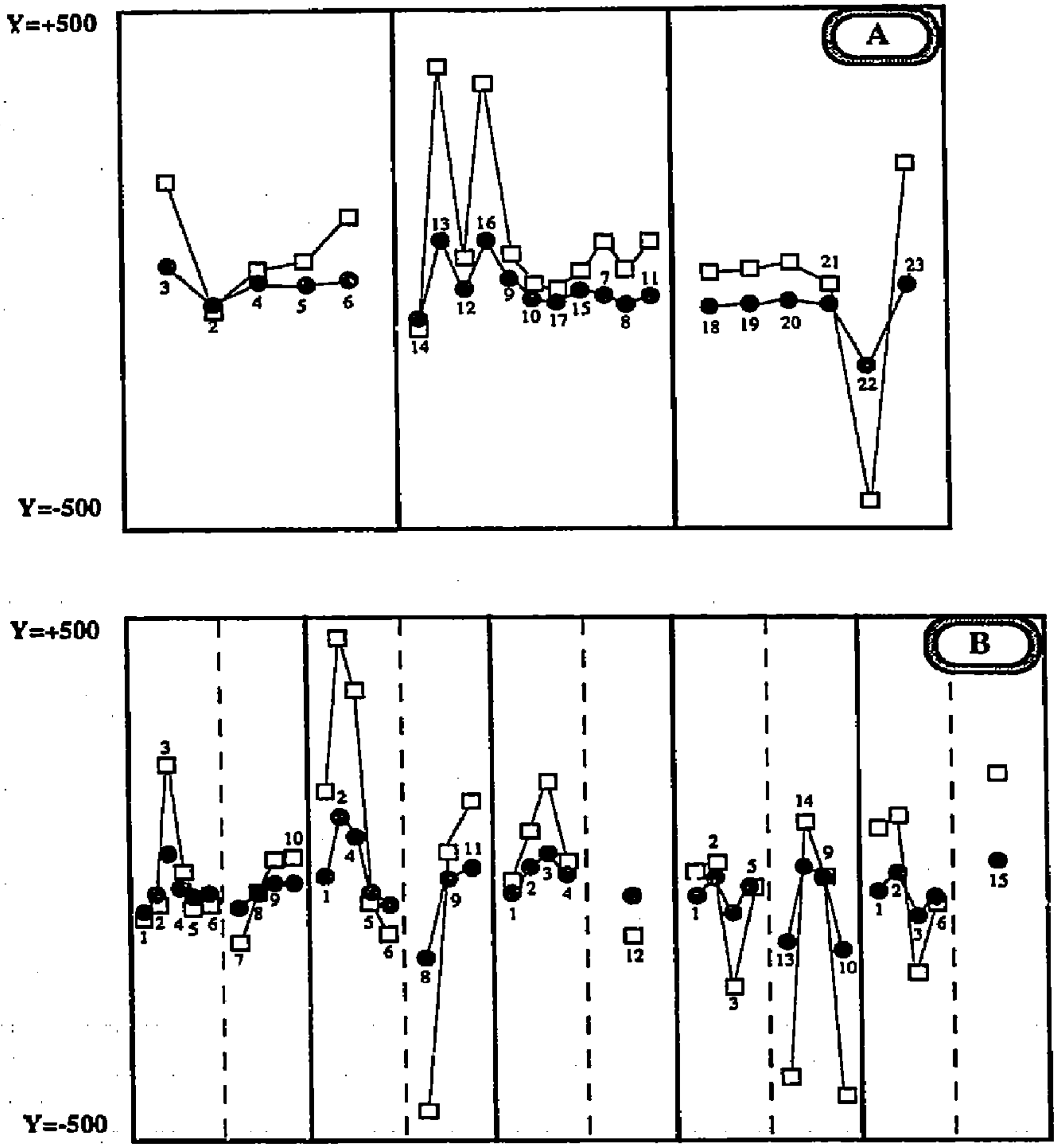

Fig. 6. Enthalpy (●) and entropy (☐) change patterns (Y in kJ mol^{-1} or kJ mol^{-1} K^{-1} respectively) for the overall (A) and stepwise (B) Ag(I) complex formation in aqueous solution and ionic strength $\mu = 1$ for KNO$_3$. In A the numbers correspond to the complex produced in B to the reacting substratum: 1, Ag(I); 2, AgTu$^+$; 3, AgTa$^+$; 4, AgCl; 5, AgBr; 6, AgI; 7, AgCl$_2^-$; 8, AgBr$_2^-$; 9, AgBrTu; 10, AgBrTa; 11, AgI$_2^-$; 12, AgClTu; 13, AgTuTa$^+$; 14, AgTu$_2^+$; 15, AgITa; 16, AgClTa; 17, AgITu; 18, AgCl$_2$Tu; 19, AgBrTu$_2$; 20, AgBrTuTa; 21, AgBr$_2$Tu$^-$; 22, AgBr$_2$Ta$^-$; 23, AgI$_2$Ta$^-$.

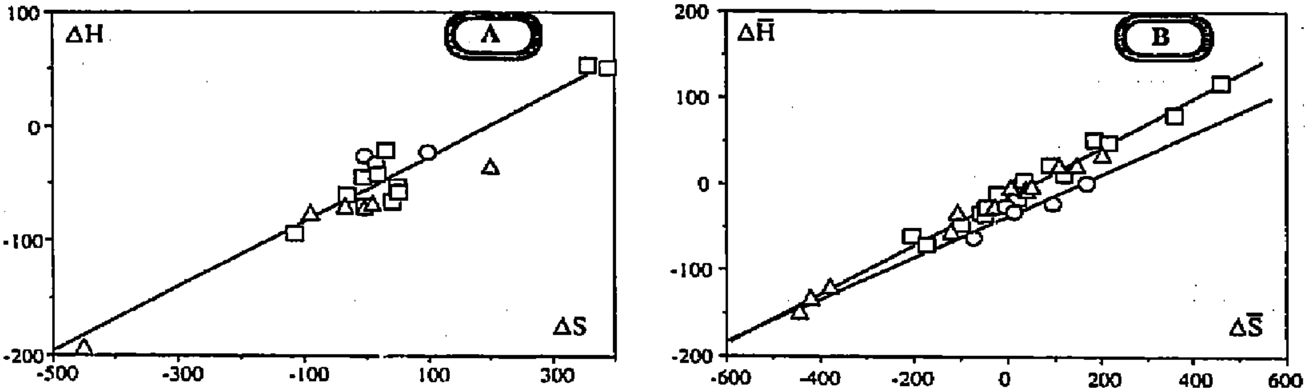

Fig. 7. Enthalpy–entropy changes ($\mathrm{kJ\,mol^{-1}}$ and $\mathrm{kJ\,mol^{-1}\,K^{-1}}$) relationships in Ag(I) overall (A) and stepwise (B) complex formation reactions in aqueous solution and ionic strength $\mu = 1$ for KNO_3: ○, formation of monocoordinates; □, formation of bicoordinates; △, formation of tricoordinates. Least-squares-fitted enthalpy–entropy change straight lines:

A: $\Delta H = -54.67(\pm 3.4) + 0.283(\pm 0.02)\Delta S$; $R = 0.951$; $T_{iso} = 283$ K

B: $\Delta \bar{H} = -38.38(\pm 5.2) + 0.238(\pm 0.05)\Delta \bar{S}$; $R = 0.928$; $T_{iso} = 238$ K

$\Delta \bar{H} = -14.43(\pm 1.2) + 0.284(\pm 0.01)\Delta \bar{S}$; $R = 0.993$; $T_{iso} = 284$ K

The linear enthalpy–entropy relationship imposes the occurrence of linear free energy–enthalpy and free energy–entropy relationships (not reproduced in the diagram) whose least-squares equations are:

A: $-\Delta G = 54.87(\pm 3.38) + 0.014(\pm 0.02)\Delta S$; $R = 0.153$

$-\Delta G = 52.85(\pm 4.68) - 0.05(\pm 0.07)\Delta H$; $R = 0.159$

B: $$\left.\begin{aligned}-\Delta \bar{G} &= 38.50(\pm 5.07) + 0.061(\pm 0.05)\Delta \bar{S};\ R = 0.549\\ -\Delta \bar{G} &= 43.50(\pm 8.83) + 0.086(\pm 0.25)\Delta \bar{H};\ R = 0.198\end{aligned}\right\}\text{lower trend}$$

$$\left.\begin{aligned}-\Delta \bar{G} &= 14.51(\pm 1.24) + 0.132(\pm 0.01)\Delta \bar{S};\ R = 0.359\\ -\Delta \bar{G} &= 14.94(\pm 1.34) + 0.031(\pm 0.02)\Delta \bar{H};\ R = 0.224\end{aligned}\right\}\text{upper trend}$$

interdependence indicates (Fig. 7) a single compensative linear relationship for the complexive parameters (Fig. 7A), while the stepwise parameters give rise to two linear compensative trends which discriminate between Ag(I) (Fig. 7B, lower trend) and mono- and bicoordinated substrata (Fig. 7B, upper trend).

In the formation of monocoordinates (Ag(I) + L = AgL), the differences between thioacetamide and thiourea (though both thione ligands) is sharp. They give rise to different enthalpy changes and, owing to the close coupling of ΔH and ΔS, different entropy changes. Both enthalpy and entropy changes for the formation of $AgTu^+$ are negative. The reaction $Ag(I) + Ta = AgTa^+$ is virtually athermic ($\Delta H \approx 0$) but exhibits a favourable ΔS value.

In the reaction of thiourea or thioacetamide with monocoordinates ($AgW + L = AgWL$, L = Tu or Ta, W = Cl^-, Br^-, I^-), the enthalpy (entropy) changes decrease systematically following the order $AgTu^+$

> AgCl > AgBr > AgI which is the exact reverse of the order for the enthalpy changes for the formation of the above monocoordinated complexes. The greater (lower) the enthalpy change for the formation of monocoordinate, the lower (greater) the enthalpy change for the single ligand coordination reaction with monocoordinated substrata.

The halide ligands Cl^-, Br^-, I^- exhibit about the same thermal tonalities in the formation of AgL, with I^- showing higher, positive entropy change.

In the reaction for the formation of bicoordinates (AgW + L = AgWL, where L is Cl^-, Br^-, I^-, W is Tu, Ta), the enthalpy changes increase with the enthalpy changes for the formation of AgW.

CONCLUSIONS

The reported results confirm the reliability of the proposed exponential model to describe the relationship between substratum-to-ligand affinities and the complexive thermodynamic stabilities of the reacting substrata. Of course, the model does not fit all such relationships but the conditions for its application, together with the eventual discriminating ability between monocoordinated and bicoordinated substrata, must be verified [4].

The parameters A, B and C for thioacetamide and the other previously reported entering groups need qualitative improvement using a more suitably distributed data set. This is especially true for the parameter C for whose precise quantitative definition (value) it is necessary to fill the gap between the independent variable $-\Delta G = 0$ and $-\Delta G = 25\ \mathrm{kJ\ mol^{-1}}$, corresponding to coordination reactions for complex substrata whose thermodynamic stabilities are lower than that of AgCl.

Owing to the nature of the donor atom of both thiourea and thioacetamide, the same coordination number can be assumed for the two-ligand system with the same central ion. Actually in only one case does the behaviour of the experimental points of the titrations need the introduction of a species $AgTa_2^+$ to explain the experimental behaviour (system Ag(I)–Tu–Ta–I^-, $T = 10°C$, $\mu = 1$ for KNO_3, $\log \beta_2$ for $AgTa_2^+ = 12$).

From the values for A, B and C reported in the caption of Fig. 4, $\Delta G = -16.7\ \mathrm{kJ\ mol^{-1}}$ can be calculated for the reaction $AgTa^+ + Ta = AgTa_2^-$, and then a complexive $\Delta G = -65.69\ \mathrm{kJ\ mol^{-1}}$ for the reaction $Ag(I) + 2Ta = AgTa_2^+$ corresponding to $\log K_2 = 2.93$ and $\log \beta_2 = 11.49$ at 25°C and $\mu = 1$. At different temperatures, the estimated $\log \beta_2$ values are in sufficient agreement with the experimental value at 10°C. From this value, $\alpha = \beta_2[Ta]^2/(1 + \beta_1[Ta] + \beta_2[Ta]^2) = 4.14 \times 10^{-3}$ is calculated for $AgTa_2^+$, a value too low to be recorded in our experiments. Similarly, for the complexive formation of AgClTuTa or AgBrTuTa, with the data from Fig. 5 and the complexive thermodynamic stabilities of AgClTu or AgBrTu from Table 2, $\log \beta = 11.31$ and 12.21 are estimated for the two three-ligand complexes, respectively. Also these values are readily comparable with the data in Table 1.

Although the ligands investigated span a very large range of softness [9], the well-defined enthalpy–entropy (and consequently the free energy–entropy and free energy–enthalpy) compensative relationship demonstrates a single mechanism [6, 10] for the metal-to-ligand interactions, both in the coordination to solvated Ag(I) and in the coordination to monocoordinated or bicoordinated substrata, independent of the coordination level.

In the trend related to the first coordination of Ag(I), thiourea and thioacetamide, ligands of similar softness, lie at the two extremes of the data set (Fig. 7B, lower trend). The iodide ion, the softest among the halide series, is differentiated from chloride by more (less) favourable entropy (enthalpy) changes. The point distribution on the trend, related to the softness of the ligands, confirms [12, 13] that in aqueous solution unfavourable (favourable) entropy (enthalpy) changes do not necessarily correspond to soft–soft interactions.

Assuming that the *C* parameter of the proposed exponential model ($Y = A + B\exp(-CX)$) is a semi-empirical softness parameters (a lower *C* value corresponds to higher softness), the softness in aqueous solution at 25°C and $\mu = 1$ of these and the previously investigated ligands follows the order $\text{Cl}^- < \text{Br}^- < \text{Tu} \approx \text{S}_2\text{O}_3^{2-} < \text{SCN}^-(?) < \text{Ta} < \text{I}^- < \text{NH}_3(?)$.

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