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Thermodynamics of complex formation of Ag(I). Part 10. Investigations on complex equilibria between Ag(I) and thioureas in ethanol

Domenico De Marco*, Antonino Giannetto, Francesco Barone,
Alessandro Visco

Department of Inorganic Chemistry, Analytical Chemistry and Molecular Structure,
University of Messina, Salita Sperone 31, 98166 S. Agata (Messina), Italy

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Abstract

The complex equilibria between Ag(I) and thiourea or *N*-alkyl-substituted thioureas have been investigated in ethanol by potentiometry at different temperatures in the range 0–45°C. The free energy, enthalpy and entropy changes at 25°C and ionic strength $\mu = 0$ for the formation of mono-, bi- and tri-coordinate compounds are given.

The investigated alcohols favour the complex formation, but specific factors operate on the transfer of each reaction from water to methanol to ethanol. Interaction between tetramethylthiourea and Ag(I) involves a different mechanism compared with the other thioureas owing to the different electronic structure of the ligand.

The ranked affinity sequences of the ligands follow different orders according to the coordination level of the substratum.

Keywords: Enthalpy–entropy relationship; Equilibrium; Ethanol; Isoequilibrium; Silver ion; Thiourea

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1. Introduction

The manifold proposed solvent classifications based on this or that chemical, physical or physico-chemical property [1–10], most of them even strictly correlated

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* Corresponding author.

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[1,11,12], provide implicit evidence of the clear role [11–19] of the solvent medium in chemical reactions.

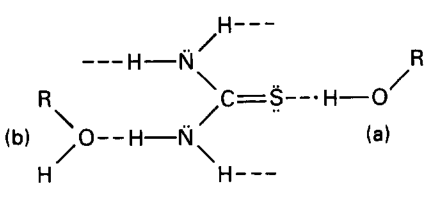
Thiourea and its *N*-substituted derivatives have both acceptor and donor strong sites. The hydrogen atoms of the amide groups act as acceptors, and both the sulphur and the nitrogen atoms can act as donor depending on the reaction partner [20,21]. The coordinate bond formed by the sulphur atom involves σ electron donation from ligand to metal ion and also π back-donation from metal ion to ligand when the electronic structure of the acceptor allows [22,24].

The energy levels of the σ electrons and of the empty π^* orbitals of the thiocarbonyl group $>\mathrm{C}{=}\ddot{\underset{\cdot\cdot}{\mathrm{S}}}$ are affected simultaneously, and in the same direction, by the groups attached to the carbon atom [25–27], so that groups enhancing the σ donor strength of the thiocarbonyl sulphur at the same time reduce its π acceptor ability and vice versa. It follows that the effects, being opposite, mutually compensate as a rough approximation, and no great changes are to be expected in the strength of the coordinate bond.

Metal ions (acceptors) with many peripheral electrons and a low oxidation state (those designated as soft according to Pearson) coordinate thiocarbonyl ligands by a σ bond and π back-bond mechanism. The straightforward conclusion of such a premise is that the substitution of one or more hydrogen atoms of thiourea with radicals cannot produce any great change in the sulphur-to-metal ion bond strength.

Water and alcohols are at the same time strong acceptor and donor solvents. Inorganic cations M^{n+} are solvated exclusively through the donor atom (or atoms) of the solvent $(\mathrm{M}^{n+}\text{–}\mathrm{O}{<}^{\mathrm{R}}_{\mathrm{H}})$.

Thiourea and related ligands can be solvated at their acceptor and donor centres. The amide hydrogens are solvated via the oxygen atom of the solvent and the nitrogen or sulphur is solvated via hydrogen. As the solvation of the nitrogen atoms of the thioureas is energetically disfavoured because of the conjugation of the lone pair with the thiocarbonyl group, the solvation of thiourea occurs according to Scheme 1.



(1)

Bearing in mind such a model for the solvation, the metal ion-to-ligand coordination reactions in solution involve the following steps.

1. Displacement of the solvent molecules bound as donors to the central metal ion (acceptor) and displacement of the solvent molecules bound as acceptors to the donor atom of the ligand ((a) in Scheme 1).
2. Metal ion-to-ligand interactions.

3. Reinforcement of the bond strength between the acceptor sites of the coordinated ligand and the solvent molecules ((b) in Scheme 1).

4. Solvent–solvent interactions between the ejected solvent molecules for the metal ion-to-ligand coordination and the solvent molecules in bulk.

5. Steric hindrance in the presence of bulky groups attached to the amide moiety and/or to the solvent molecule. This steric hindrance prevents an otherwise more effective solvent stabilization of the produced complex.

As these steps are arbitrary divisions of a unitary process, there is a very strict interplay among them, and it is wrong to consider separately the influence of each step on complex formation.

The present contribution refers to the results of investigations on complex equilibria between Ag(I) and thioureas in ethanol. Previously the same equilibria have been investigated in methanol [28] and in aqueous solution [29]. Note that charges are omitted throughout.

2. Experimental

2.1. Chemicals

Commercial ethanol (water content $< 0.1\%$). The ligands were commercial products (purity $> 98\%$) and were used without further purification. $AgNO_3$ was used as the source of the Ag(I) solutions in ethanol. The solutions were prepared by direct weighing.

The investigated concentration ranges were:

$$1.0 \times 10^{-5}\ \mathrm{M} \leqslant [\mathrm{Ag(I)}]_{\mathrm{tot}} \leqslant 5.0 \times 10^{-5}\ \mathrm{M}\ \text{(five different concentrations);}$$

$$1.33 \times 10^{-4}\ \mathrm{M} \leqslant [\mathrm{ligand}]_{\mathrm{tot}} \leqslant 1.8 \times 10^{-3}\ \mathrm{M}\ \text{(ten different concentrations).}$$

A self determined ionic medium was used for $AgNO_3$ concentration. The $\Delta E = E_{\mathrm{cal}} - E_{\mathrm{exp}}$ values were extrapolated to $[AgNO_3]_{\mathrm{tot}} = 0$ and the figures in Tables 1–4 refer to ionic strength $\mu = 0$.

2.2. Methods

Potentiometry

The measuring cell had the composition

Ag (test Elec.)	$[AgNO_3]_{tot}$ = Const. $[Ligand]_{tot}$ = Var in Ethanol	$LiNO_3$ sat. Salt Bridge in Ethanol	KCl Sat. Aqueous Solution	Ag (ref. Elec.)

The measurements were performed in a thermostated room. Details on the processing of the experimental data can be found in Refs. 28 and 29, or can be obtained from the authors.

Table 1

Stability constants $\log\beta$ and free energy changes ΔG (in kJ mol^{-1}) for the overall complex formation between Ag(I) and thiourea or N-substituted thioureas at various temperatures and ionic strength $\mu = 0$ in ethanol

Ligand	n	$t = 0$°C		$t = 5$°C		$t = 10$°C		$t = 15$°C		$t = 20$°C	
		$\log\beta$	$-\Delta G$	$\log\beta$	$-\Delta G$	$\log\beta$	$-\Delta G$	$\log\beta$	$-\Delta G$	$\log\beta$	$-\Delta G$
Tu	1	–	–	9.05 ± 0.05	48.2	–	–	9.48 ± 0.2	52.84	–	–
	2	–	–	13.16 ± 0.05	70.10	–	–	13.35 ± 0.01	73.62	–	–
	3	–	–	17.74 ± 0.1	94.45	–	–	17.08 ± 0.05	94.23	–	–
MeTu	1	11.52 ± 0.2	60.89	8.58 ± 0.05	45.67	–	–	9.24 ± 0	50.98	–	–
	2	13.27 ± 1	70.17	14.04 ± 0.05	74.74	–	–	13.78 ± 0.1	76.04	–	–
	3	17.86 ± 0.05	94.41	16.93 ± 0.1	90.15	–	–	–	–	–	–
Me_2Tu	1	–	–	9.03 ± 0.02	48.1	9.49 ± 0.01	51.46	8.33 ± 0.03	45.93	9.37 ± 0.02	52.60
	2	–	–	13.03 ± 0.01	71.47	13.19 ± 0.01	71.47	12.30 ± 0.03	67.85	13.10 ± 0.02	73.51
	3	–	–	16.94 ± 0.1	90.22	16.46 ± 0.05	89.20	16.13 ± 0.1	89.00	16.40 ± 0.1	92.06
Me_4Tu	1	4.55 ± 0.05	23.82	7.25 ± 0.05	38.62	3.99 ± 0.05	21.64	4.52 ± 0.05	24.94	3.57 ± 0.05	20.06
	2	8.64 ± 0.05	45.27	9.67 ± 0.05	51.48	9.56 ± 0.2	51.84	8.61 ± 0.02	47.48	9.82 ± 0.1	55.08
	3	13.27 ± 0.1	69.49	12.94 ± 0.01	67.48	12.41 ± 0.05	68.28	12.93 ± 0.1	71.32	–	–
EtTu	1	–	–	10.77 ± 0.03	57.35	10.20 ± 0.15	55.28	9.62 ± 0.02	53.04	11.0 ± 0.4	61.91
	2	–	–	14.51 ± 0.03	77.24	12.07 ± 0.5	65.45	13.43 ± 0.02	74.10	14.30 ± 0.02	80.26
	3	–	–	17.68 ± 0.1	94.12	15.31 ± 0.15	82.99	16.58 ± 0.1	91.45	16.79 ± 0.06	94.20
Et_2Tu	1	–	–	9.37 ± 0.03	49.91	9.68 ± 0.1	52.45	9.18 ± 0.03	50.65	8.16 ± 0.05	45.77
	2	–	–	13.21 ± 0.03	70.35	13.50 ± 0.1	73.19	12.97 ± 0.03	71.51	12.59 ± 0.05	70.66
	3	–	–	16.61 ± 0.2	88.46	–	–	16.53 ± 0.05	91.18	15.63 ± 0.3	87.72
EnTu	1	10.23 ± 0.05	53.57	–	–	10.05 ± 0.01	54.48	–	–	10.02 ± 0.03	56.23
	2	14.80 ± 0.05	77.52	–	–	13.92 ± 0.1	75.48	–	–	14.03 ± 0.05	78.73
	3	17.98 ± 0.1	94.17	–	–	17.50 ± 0.15	94.87	–	–	–	–
ALTu	1	11.07 ± 0.2	57.96	–	–	11.17 ± 0.05	60.53	–	–	9.98 ± 0.1	56.01
	2	14.59 ± 0.05	76.63	–	–	14.05 ± 0.1	76.16	–	–	13.65 ± 0.1	76.63
	3	18.03 ± 0.1	94.45	–	–	17.11 ± 0.1	92.73	–	–	16.9 ± 0.2	94.48
$IsPr_2Tu$	1	9.61 ± 0.01	50.34	–	–	9.4 ± 0.05	50.97	–	–	9.8 ± 0.01	55.01
	2	13.37 ± 0.05	70.02	–	–	13.2 ± 0.1	71.64	–	–	13.30 ± 0.02	74.63
	3	15.90 ± 0.1	83.25	–	–	16.76 ± 0.1	90.87	–	–	16.31 ± 0.03	91.52
Bu_2Tu	1	10.39 ± 0.1	54.43	–	–	9.45 ± 0.05	51.25	–	–	10.03 ± 0.02	56.28
	2	14.75 ± 0.1	77.27	–	–	13.25 ± 0.05	71.83	–	–	13.13 ± 0.03	73.56
	3	–	–	–	–	17.30 ± 0.1	93.79	–	–	16.32 ± 0.1	91.57

Ligand	n	$t = 25$°C		$t = 30$°C		$t = 35$°C		$t = 40$°C		$t = 45$°C	
		$\log\beta$	$-\Delta G$	$\log\beta$	$-\Delta G$	$\log\beta$	$-\Delta G$	$\log\beta$	ΔG	$\log\beta$	ΔG
Tu	1	8.69 ± 0.05	49.58	–	–	7.35 ± 0.05	44.55	9.77 ± 0	58.56	8.89 ± 0.05	54.17
	2	13.34 ± 0.1	76.13	–	–	12.77 ± 0.2	75.35	13.22 ± 0.2	79.28	12.77 ± 0.05	77.79
	3	16.24 ± 0.2	92.71	–	–	–	–	–	–	–	–
MeTu	1	9.22 ± 0.05	52.60	–	–	8.44 ± 0.05	49.81	11.01 ± 0.1	66.03	9.19 ± 0.05	56.00
	2	13.20 ± 0.05	75.36	–	–	13.02 ± 0.1	76.78	14.02 ± 0.1	84.04	12.9 ± 0.2	78.56
	3	–	–	–	–	–	–	16.81 ± 0.06	100.6	–	–
Me_2Tu	1	8.19 ± 0.02	46.75	8.06 ± 0.05	46.48	8.79 ± 0.01	51.86	4.68 ± 0.02	28.04	4.66 ± 0.03	28.38
	2	12.07 ± 0.01	68.91	11.91 ± 0.05	69.11	12.32 ± 0.05	72.69	9.98 ± 0.15	55.64	8.86 ± 0.1	53.74
	3	15.46 ± 0.3	88.22	15.45 ± 0.15	89.58	–	–	–	–	–	–
Me_4Tu	1	4.56 ± 0.3	26.03	–	–	4.29 ± 0.01	25.31	10.85 ± 0.1	65.06	10.13 ± 0.01	61.69
	2	9.4 ± 0.01	53.67	–	–	8.18 ± 0.01	48.24	12.67 ± 0.6	75.97	13.56 ± 0.03	82.58
	3	–	–	–	–	11.95 ± 0.05	70.48	15.95 ± 0.15	95.6	–	–
EtTu	1	9.35 ± 0.04	53.40	10.83 ± 0.1	62.86	9.27 ± 0.03	54.67	7.44 ± 0.03	44.60	–	–
	2	14.06 ± 0.04	80.27	13.74 ± 0.01	79.75	13.56 ± 0.1	79.99	11.54 ± 0.03	69.18	–	–
	3	–	–	16.40 ± 0.1	95.20	–	–	15.4 ± 0.15	92.32	–	–

Table 1 (continued)

Ligand	n	$t = 25°C$		$t = 30°C$		$t = 35°C$		$t = 40°C$		$t = 45°C$	
		$\log \beta$	$-\Delta G$	$\log \beta$	$-\Delta G$	$\log \beta$	$-\Delta G$	$\log \beta$	$-\Delta G$	$\log \beta$	$-\Delta G$
Et_2Tu	1	9.61 ± 0.02	54.83	8.40 ± 0.01	48.77	–	–	8.43 ± 0.02	50.51	–	–
	2	11.99 ± 0.05	68.42	12.63 ± 0.03	73.32	–	–	12.83 ± 0.02	76.91	–	–
	3	16.07 ± 0.1	91.72	13.54 ± 0.08	89.05	–	–	–	–	–	–
EnTu	1	–	–	9.03 ± 0.05	52.43	–	–	–	–	–	–
	2	–	–	13.32 ± 0.04	77.30	–	–	–	–	–	–
	3	–	–	–	–	–	–	–	–	–	–
ALTu	1	–	–	9.19 ± 0.02	53.33	–	–	9.85 ± 0.02	59.05	–	–
	2	–	–	11.96 ± 0.05	69.44	–	–	13.00 ± 0.05	77.93	–	–
	3	–	–	13.40 ± 1.0	77.76	–	–	–	–	–	–
$IsPr_2Tu$	1	–	–	9.62 ± 0.02	55.85	–	–	9.85 ± 0.03	59.02	–	–
	2	–	–	13.23 ± 0.05	76.80	–	–	12.95 ± 0.05	77.46	–	–
	3	–	–	15.99 ± 0.45	92.78	–	–	15.29 ± 0.11	91.65	–	–
Bu_2Tu	1	–	–	8.39 ± 0.03	48.67	–	–				
	2	–	–	12.19 ± 0.0	70.75	–	–				
	3	–	–	15.80 ± 0.2	91.72	–	–				

3. Results

Table 1 refers to the identified complexes, the stability constants and the free energy changes as obtained for the overall complex formation directly from the experimental data.

Table 2 gives the linearly interpolated ΔG values at 25°C, the corresponding $\log \beta$ and the enthalpy and entropy changes deduced from the linear dependence of the ΔG of Table 1 on temperature.

Table 3 shows the stepwise thermodynamic parameters deduced from Table 2.

In order to give a comprehensive and immediate view of the thermodynamic behaviour of the identified equilibria, the linear relationships ΔG vs. T with the data of Table 3 for the stepwise equilibria are reproduced in Fig. 1(A) so that the enthalpy and entropy changes are simultaneously represented by the intercepts and slopes of the straight lines.

Of course, the calculated ΔG values are reliable only within the investigated temperature range, and ΔH (the intercept) and ΔS (the negative slope) must be considered as the most probable values within the range.

The diagrams in Fig. 1(B) reproduce the ΔH–ΔS relationships for the same reactions as shown in Fig. 1(A). The two representations are reproduced together because they are strictly intercorrelated, for the following reasons.

(a) The diagrams of the (ΔH, ΔS) pairs reproduce the parameters of the Gibbs equation $\Delta G = \Delta H - T\Delta S$ with ΔH and ΔS invariant with temperature.

(b) The occurrence of a single intersection point for a set of coplanar straight lines implies that the intercepts and slopes are linearly interrelated, and vice versa. The parameters of the linear relationship correspond to the abscissa and ordinate of the intersection point.

Table 2

Stability constants log β_n and changes in free energy ΔG, enthalpy ΔH, and entropy ΔS, changes (in kJ mol^{-1}, kJ mol^{-1} and J mol^{-1} K^{-1} respectively) for the overall complex formation reactions of Ag(I) with thiourea or *N*-substituted thioureas in ethanol at 25°C and ionic strength $\mu = 0$ as deduced from Table 1 by least squares fitting to a straight line. The original data were smoothed by using *I* consecutive points

Ligand	*n*	log β	$-\Delta G$	ΔH	ΔS	*I*
Tu	1	9.86	56.26	-107 ± 24	-171 ± 80	3
	2	13.88	79.22	-46 ± 17	$+110 \pm 58$	3
	3	16.46	93.93	-138 ± 10	-147 ± 37	3
MeTu	1	10.12	57.59	-29 ± 24	$+97 \pm 83$	3
	2	13.81	78.80	-37 ± 15	$+140 \pm 50$	3
	3	17.23	98.34	-8 ± 2	$+302 \pm 7$	3
Me_2Tu	1	8.54	48.78	-51 ± 9	-9 ± 31	3
	2	12.36	70.54	-57 ± 8	$+46 \pm 9$	3
	3	15.75	89.93	-83 ± 8	$+25 \pm 26$	3
Me_4Tu	1	4.49	25.62	-30 ± 26	-17 ± 86	3
	2	9.08	51.83	-26 ± 5	$+85 \pm 18$	3
	3	12.37	70.61	-39 ± 2	$+106 \pm 8$	3
EtTu	1	10.54	57.97	-5 ± 14	$+177 \pm 48$	3
	2	13.56	77.41	-47 ± 24	$+243 \pm 80$	3
	3	16.41	93.71	-2 ± 21	$+308 \pm 71$	3
Et_2Tu	1	8.71	49.74	-67 ± 9	-57 ± 30	3
	2	12.36	70.57	-91 ± 9	-70 ± 32	3
	3	15.78	90.12	-64 ± 14	$+87 \pm 46$	3
EnTu	1	9.39	53.64	-79 ± 8	-85 ± 27	3
	2	13.57	77.47	-71 ± 5	$+20 \pm 16$	3
	3	–	–	–	–	–
ALTu	1	9.64	55.09	-109 ± 30	-184 ± 104	–
	2	12.71	72.57	-133 ± 36	-204 ± 124	–
	3	15.19	16.73	-210 ± 47	414 ± 163	–
$IsPr_2Tu$	1	9.7	55.36	$+12 \pm 7$	$+226 \pm 25$	3
	2	13.2	75.4	-10 ± 1	$+217 \pm 5$	3
	3	16.2	92.47	-5 ± 33	$+292 \pm 114$	–
Bu_2Tu	1	9.41	53.74	-44 ± 38	$+33 \pm 130$	3
	2	12.86	73.43	-77 ± 34	-15 ± 117	3
	3	16.15	92.20	-110 ± 11	-63 ± 39	–

Fig. 2 represents the relationships of the thermodynamic parameters ΔG and ΔH in the solvents ethanol–water and ethanol–methanol for stepwise complex formation. The vertical (horizontal) distances of the point from the bisector of the X–Y coordinates represent the actual value of the transfer parameter.

4. Discussion

In ethanol, the reactions of thiourea and substituted thioureas with Ag(I) lead to the formation of tri-coordinate complexes. The formation of tri-coordinate complexes with *N*-methylthiourea and *N*-ethylenethiourea has been found only at low

Table 3

Stability constants log K_n and changes in free energy ΔG, enthalpy ΔH and entropy ΔS (in kJ mol^{-1}, kJ mol^{-1} and J mol^{-1} K^{-1} respectively) for the stepwise complex formation reactions of Ag(I) with thiourea or *N*-substituted thioureas in ethanol at 25°C and ionic strength $\mu = 0$ as deduced from Table 2

Ligand	n	log K	$-\Delta G$	ΔH	ΔS
Tu	1	9.86	56.26	−107	−171
	2	4.02	22.96	+61	+281
	3	2.58	14.71	−92	−257
MeTu	1	10.12	57.79	−29	+97
	2	3.69	21.01	−8	+43
	3	3.42	19.54	+29	+162
Me_2Tu	1	8.54	48.78	−51	−9
	2	3.82	21.76	−6	+55
	3	3.39	19.39	−26	−21
Me_4Tu	1	4.49	25.62	−30	−17
	2	4.59	26.21	4	+102
	3	3.29	18.78	−13	+21
EtTu	1	10.54	57.97	−5	+177
	2	3.02	19.43	0	+66
	3	2.85	16.36	3	+65
Et_2Tu	1	8.71	49.74	−67	−57
	2	3.65	20.83	−24	−13
	3	3.42	19.55	+29	+157
ALTu	1	9.64	55.09	−109	−184
	2	3.07	17.48	−24	−20
	3	2.48	14.16	−77	−210
$IsPr_2Tu$	1	9.7	55.36	+12	+226
	2	3.5	20.04	−22	−9
	3	3.0	17.04	−1	+75
Bu_2Tu	1	9.41	53.74	−44	+33
	2	3.45	19.69	−33	−48
	3	3.29	18.77	−33	−48

temperature ($t < 10$°C), perhaps because higher temperatures destabilize the third complex with respect to the preceding ones.

The linear relationships ΔG vs. T for the three stepwise complexations $AgL_{n-1} + L = AgL_n$ ($n = 1$–3) identify a set of straight lines with a single common intersection point which corresponds to a linear ΔH–ΔS interplay ($\Delta H = \Delta H_{res} + \tau\Delta S$). In the first complexation reaction $Ag(I) + L = AgL$, tetramethylthiourea shows sharp divergence from the corresponding reactions with the other ligands. Its behaviour in the ΔG–T coordinates is clearly mapped in ΔH–ΔS coordinates, where the reaction with tetramethylthiourea lies outside the trend for less favourable changes in both enthalpy and entropy.

The ΔH–ΔS relationships for the three complexation reactions are substantially parallel: the single intersection points for the three sets of Gibbs lines have substantially coincident abscissas. The trend for the first complexing reactions

Table 4
Thermodynamic transfer parameters ΔG_{tr}, ΔH_{tr}, ΔS_{tr} (in kJ mol^{-1}, kJ mol^{-1} and J mol^{-1} K^{-1} respectively) from water to ethanol and from methanol to ethanol for the overall and stepwise complex formation reactions of Ag(I) with thiourea and *N*-substituted thioureas at 25°C and ionic strength $\mu = 0$

		From H_2O to C_2H_5OH					
		overall			stepwise		
Ligand	n	$-\Delta G_{tr}$	ΔH_{tr}	ΔS_{tr}	$-\Delta G_{tr}$	ΔH_{tr}	ΔS_{tr}
Tu	1	14.86	+47	+206	14.86	+47	+206
	2	18.99	+62	+260	4.16	+13	+55
	3	21.09	−57	−26	2.21	−88	−286
MeTu	1	21.29	−11	+159	21.29	−11	+34
	2	21.50	+9	+102	0	+20	+68
	3	24.24	+115	+469	2.84	+107	−43
Me_2Tu	1	14.08	−51	−126	14.08	−51	−126
	2	11.11	−39	−92	3.14	+12	+34
	3	12.53	−37	−79	1.39	+2	+54
Me_4Tu	1	−6.98	−24	−105	−6.98	−24	−105
	2	−2.57	−6	−32	4.51	+18	+73
	3	−3.90	−2	−19	−1.32	+4	+13
EtTu	1	21.57	+50	+239	21.57	+50	+115
	2	16.71	+103	+404	−4.8	+5	+166
	3	15.41	+132	+578	−1.24	+28	+174
Et_2Tu	1	16.24	+21	+149	16.24	+21	+149
	2	18.67	−7	+31	2.43	−28	+118
	3	21.02	+25	+152	2.45	+34	+121
EnTu	1	21.44	−48	−89	21.44	−48	−89
	2	22.17	−19	+30	0.8	+13	+120
	3	–	–	–	–	–	–
ALTu	1	16.99	−129	−241	16.99	−129	−241
	2	13.37	+67	+141	−3.42	−110	−206
	3	6.33	−148	−432	−6.37	−119	−290

		From CH_3OH to C_2H_5OH					
		overall			stepwise		
Ligand	n	$-\Delta G_{tr}$	ΔH_{tr}	ΔS_{tr}	$-\Delta G_{tr}$	ΔH_{tr}	ΔS_{tr}
Tu	1	7	+20	+90	7	+20	+90
	2	−4.5	+20	+86	−2.5	0	−4
	3	3	−20	−55	−1.6	−40	−141
MeTu	1	7.5	+27	+78	7.5	27	+78
	2	2.3	−123	−404	−5.1	−150	−492
	3	6.8	+120	+425	4.4	+243	+849
Me_2Tu	1	−1.2	−14	−53	−1.3	−14	−53
	2	−0.9	+3	+10	−0.3	+17	+63
	2	2.9	+27	+102	3.8	+24	+92
Me_4Tu	1	−19	+4	−26	−11	+4	+26
	2	−3.6	−6	+8	7.3	+2.6	+34
	3	−1.21	−7	−27	2.4	−17	−35

Table 4 (continued)

		From CH_3OH to C_2H_5OH					
		overall			stepwise		
Ligand	n	$-\Delta G_{tr}$	ΔH_{tr}	ΔS_{tr}	$-\Delta G_{tr}$	ΔH_{tr}	ΔS_{tr}
EtTu	1	1.01	+34	+119	1.01	+34	+119
	2	−0.1	+80	+268	−1.17	+45	+149
	3	0.2	+118	+316	0.36	+38	+128
Et_2Tu	1	−1.9	−69	−237	−1.96	−69	−237
	2	−4.6	−69	−396	−2.7	−44	−159
	3	−1.3	−17	−61	3.25	+98	+335
EnTu	1	3.9	−66	−208	3.9	−66	−208
	2	5.7	−27	−74	1.43	+39	+124
	3	–	–	–	–	–	–
ALTu	1	0	−33	+133	0	−33	−113
	2	−6.7	−51	−194	−6.5	−18	−81
	3	−7.4	−105	−377	−0.6	−40	−183
$IsPr_2Tu$	1	7.5	+94	+341	−7.5	+94	+341
	2	6.2	+47	+176	−6.5	−47	−176
	3	5.0	+112	+391	+1.16	+59	+215

Ag(I) + L = AgL is sharply distinguished from the others for more favourable ΔH_{res} ($\Delta S_{res} = \Delta H_{res}/\tau$) (the ordinate of the single intersection point in the Gibbs lines for the reaction series Ag(I) + L = AgL is more favourable when compared with the others), whereas the values of ΔH_{res} for the second and third stepwise complexation series are practically identical ($\Delta H_{res(1st\ compl.)} \ll \Delta H_{res(2nd\ compl.)} \approx \Delta H_{res(3rdcompl.)}$).

The comparison of the stepwise reactions in water, methanol and ethanol does not reveal parallelism of the behaviour in the investigated solvents, and no apparent regularity can be deduced in the values of the transfer energies even though the ΔH values in the three solvents lie approximately on the bisectors of the diagrams (Fig. 2).

5. Conclusions

The premise concerning the multifacet intervention of the solvent medium in the complexation reactions of Ag(I) with thioureas is further strengthened by the results of the present investigations. One is entitled to conclude this because of the lack of meaningful direct correlations between the thermodynamic parameters in the investigated solvents and the apparent irregularity in the transfer energies.

In any classification scale, the relative position of a given set of solvents (in the present case H_2O, CH_3OH and C_2H_5OH) is identified by a single sequence (different scales can give different sequences). On the basis of the heats of transfer from water to methanol to ethanol, the stepwise complexation reactions can be organized at least in three different ways with respect to their qualitative behaviour,

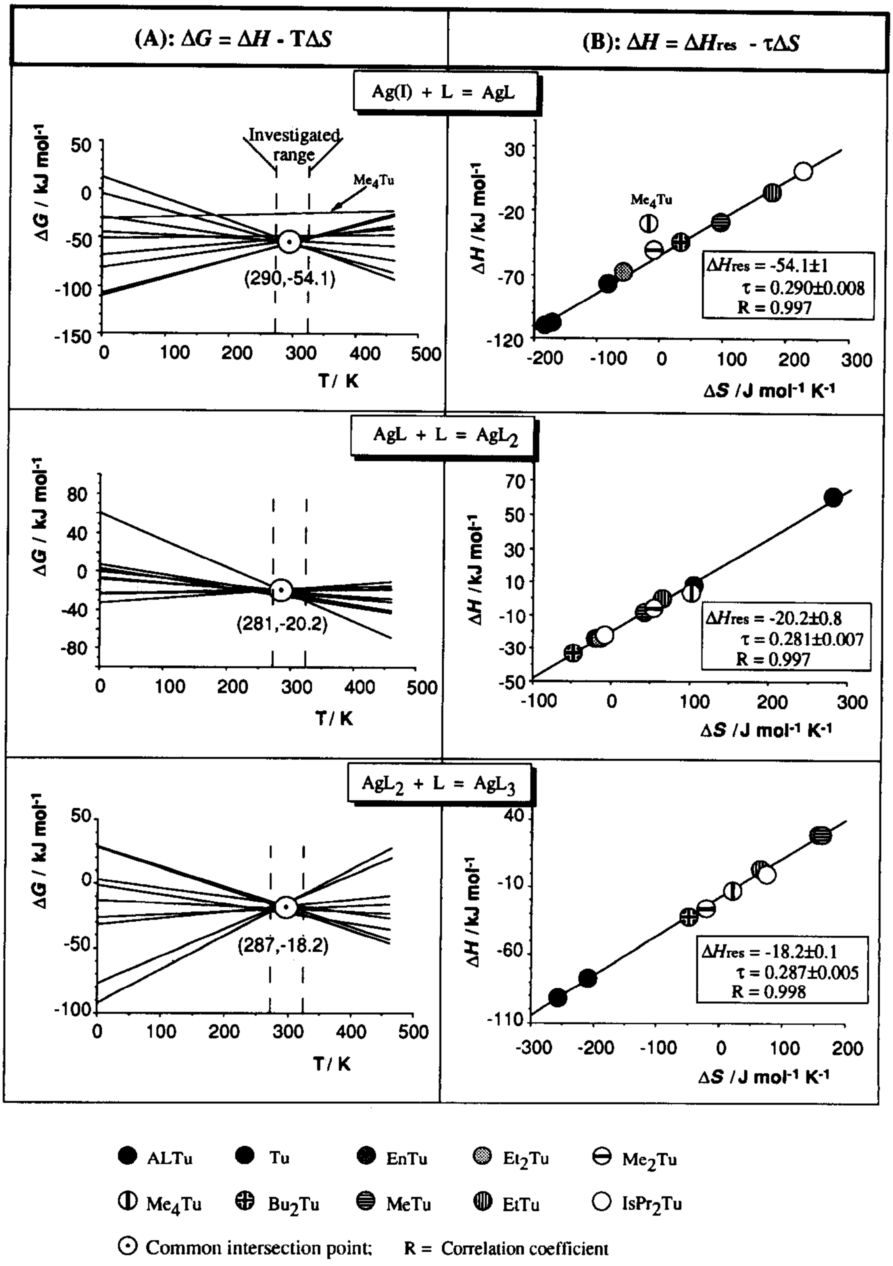


Fig. 1. ΔG vs. T (A) and ΔH vs. ΔS (B) relationships for the stepwise complex equilibria between Ag(I) and thiourea or substituted thioureas in ethanol at $t = 25°C$ and ionic strength $\mu = 0$. Affinity sequence according to the reaction $AgL_{n-1} + L = AgL_n$. For $n = 1$: ALTu < Tu < EnTu < Et_2Tu < Me_2Tu < Bu_2Tu < MeTu < EtTu < $IsPr_2Tu$. For $n = 2$: Bu_2Tu < ALTu ≈ Et_2Tu ≈ $IsPr_2Tu$ < MeTu ≈ Me_2Tu ≈ EtTu < EnTu < Tu. For $n = 3$: Tu < ALTu < Bu_2Tu ≈ Me_2Tu < EtTu ≈ $IsPr_2Tu$ < MeT ≈ Et_2Tu.

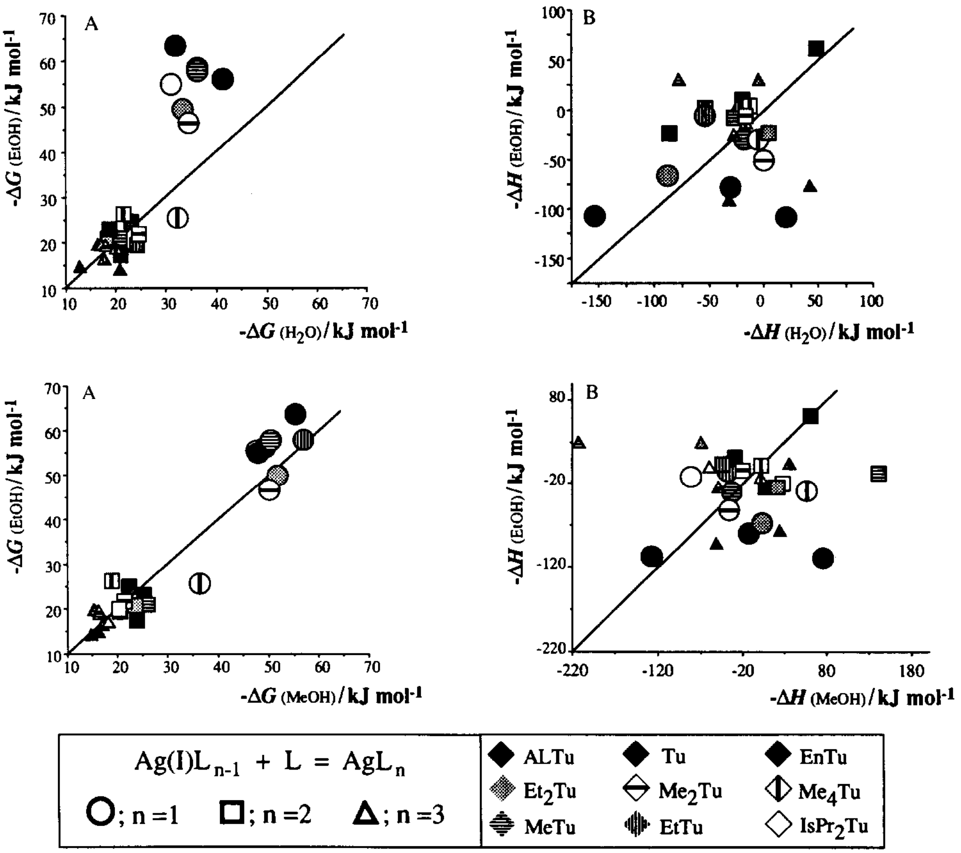


Fig. 2. Relationships between the free energy (A) or enthalpy changes (B) for the stepwise equilibria in the solvents ethanol–water and ethanol–methanol. The transfer energies are strictly dependent on the specific equilibrium.

so that it is not possible straightforwardly to use a sole criterion for interpreting or rationalizing the transfer processes from one solvent to another.

Despite the absence of meaningful parallelisms in a detailed analysis, it may be noted that the reaction heats lie in comparable ranges, and the experimental points in Fig. 2 are almost symmetrically distributed near the bisector, especially for a comparison of the reactions in methanol and ethanol.

The isoequilibrium relationships for a given homologous series (first, second or third stepwise complexing reactions) show (i) about the same value of mutual sensitivity of one parameter in respect to the other, and (ii) the same value of ΔH_{res} (ΔS_{res}) for the same reaction series in methanol [28] and ethanol, but markedly more favourable than in water [29]. Hence methanol and ethanol, in comparison with water, favour the formation of Ag(I)–thiourea complexes and influence each reaction with specific factors, some of them probably due to spatial phenomena for bulky groups carried on the ligand and/or on the solvent molecule.

The isoequilibrium relationships can be used for identifying "sensu latu" homologous reaction series (i.e. reactions between reactants different in nature but showing a single $\Delta H - \Delta S$ relationship) or for characterizing homologies and differences in the behaviour of pre-established series of reactions [30–33].

The occurrence of a single common isoequilibrium point is the necessary and sufficient condition for a substratum-to-ligand mutual affinity scale that extends over a discrete interval of experimental conditions [33]. Because of the mutual binary interdependence between ΔG, ΔH and ΔS, any one of these parameters can be assumed as an estimate of the affinity in a series of homologous reactions.

Because (a) the ΔG values usually show larger variability with temperature in comparison with the variability of ΔH or ΔS, (b) the isoequilibrium point is an inversion point for the ranked sequence of ΔG values and (c) experimental errors could lead to erroneous conclusions as to the isoequilibrium conditions if the reactions are not discriminated by their ΔG, the ΔH or ΔS values must then be preferred as estimators of the affinities, and the affinity sequences coincide with the relative position in the identified trend.

The substratum-to-ligand affinities defined in this way tend to follow the opposite order when considered for the first or the second stepwise complexation reactions ($\mathrm{Ag(I)} + \mathrm{L} = \mathrm{AgL}$ or $\mathrm{AgL} + \mathrm{L} = \mathrm{AgL_2}$; see Fig. 1). This inversion, which is independent of the actual sequence, has been observed also in water and methanol and appears to be a common element in the three solvents.

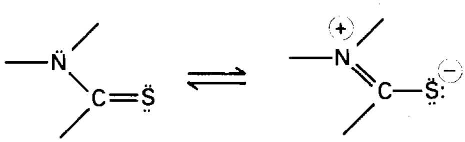
In the first coordination, thiourea always occupies the extreme position with $\Delta H < 0$ and $\Delta S < 0$, but occupies the opposite extreme in the series related to the second stepwise coordination.

In ethanol, diisopropylthiourea, a ligand with very bulky substituents, occupies the opposite extreme in respect to thiourea.

The phenomenon of inversion of the sequence can be ascribed to the intervention of the solvent molecules in the complexation reactions. In the first complex with thiourea AgTu, reinforcement of the =N–H···solvent bond of the coordinated ligand counterbalances the desolvation of the reaction sites. Hence the complex AgTu is still appreciably solvated and as a result $\Delta H < 0$ and $\Delta S < 0$. In the second stepwise coordination reaction, the positive charge of the central atom is distributed over the hydrogen atoms of the amide groups of two coordinated thiourea molecules; in comparison with AgTu the bi-coordinated $\mathrm{AgTu_2}$ has reduced stiffness, and more effective release of the coordinated solvent molecules from the solvation sphere occurs.

Compared with AgTu, the complex with diisopropylthiourea—and more generally the complexes with *N*-alkyl-substituted thioureas—are less effectively solvated because of the steric hindrance of the bulky alkyl groups. A minimum number of the solvent molecules is coordinated to the ligand and the complexing reaction will be more sensitive to temperature changes ($\Delta H > 0$ and $\Delta S > 0$).

The behaviour of the tetramethylthiourea complex $\mathrm{Ag(Me_4Tu)}$ stems from the different structure of this ligand with respect to the others. The solvent molecules cannot bind efficiently to the coordinated ligand because of a lack of amide hydrogen atoms. Moreover, the electronic structure of the "thioureide" group is resonant between the two limiting forms:



The polar formula requires coplanarity of the carbon and nitrogen σ valence hybrid orbitals. The interactions between the methyl groups of tertramethylthiourea force the nitrogen σ valence hybrid orbitals into a different plane relative to the plane defined by the carbon σ valence hybrid orbitals, favouring the apolar formula. This non-coplanarity has been evident in the molecular structure of tetramethylthiourea [34], and the prevalence of the thiocarbonyl structure can be argued by comparison of the IR spectrum to that of thiourea [35].

List of symbols

Tu	thiourea
MeTu	methylthiourea
Me_2Tu	*N,N'*-dimethylthiourea
Me_4Tu	*N,N,N',N'*-tetramethylthiourea
EtTu	ethylthiourea
Et_2Tu	*N,N'*-diethylthiourea
EnTu	ethylenethiourea
$IsPr_2Tu$	*N,N'*-diisopropylthiourea
Bu_2Tu	*N,N'*-dibutylthiourea
ALTu	allylthiourea
$[X]_{tot}$	total molar concentration of X
β_n	stability constant for the overall complexing reaction $Ag(I) + nL = AgL_n$ (in $mol^{-1}\ dm^3$)
K_n	stability constant for the stepwise complexing reaction $AgL_{n-1} + L = AgL_n$ (in $mol^{-1}\ dm^3$)
ΔG_n, ΔH_n, ΔS_n	free energy, enthalpy or entropy change (in $kJ\ mol^{-1}$, $kJ\ mol^{-1}$ and $J\ mol^{-1}\ K^{-1}$, respectively) for the overall complexing reactions
ΔG_n, ΔH_n, ΔS_n	free energy, enthalpy or entropy change (in $kJ\ mol^{-1}$, $kJ\ mol^{-1}$ and $J\ mol^{-1}\ K^{-1}$, respectively) for the stepwise complexing reactions

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