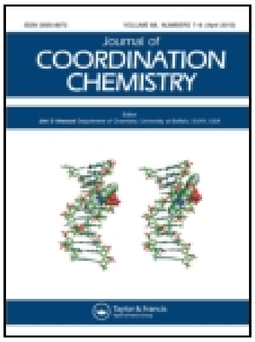

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# Thermodynamics of complex formation equilibria between Ag(I) and thiocarbonyl ligands in propan-2-one (acetone) solution

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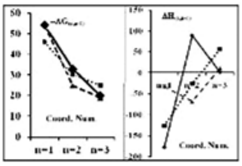
Reaction: $AgL_{(n-1)} + L = AgL_n$

Solid line: L = Thiourea;
dotted line: L = N,N'-diethylthiourea;
dashed line: L = N-phenylthiourea.

Solvent : propan-2-one.



Complex formation equilibria in propan-2-one between Ag(I) and thiourea (Tu), thioacetamide (Ta), N-methylthiourea (MeTu), N-ethylthiourea (EtTu), N,N′-diethylthiourea ($Et_2Tu$), N-phenylthiourea (PhTu), N, N′-diphenylthiourea ($Ph_2Tu$), and thiobenzanilide (TbAn) have been investigated by potentiometry at different temperatures $t$ = 0–20 °C and self-determined ionic medium. Formation of mono-, bis-, and tris-coordinated $AgL_n$ complexes (charges are omitted) has been detected, but for Ag(I)–$Ph_2Tu$ system, where the occurrence of the mono-coordinate $AgPh_2Tu$ and bis-coordinate $Ag(Ph_2Tu)_2$ has been found. The stability constants have been deduced. The standard enthalpy and entropy changes have been evaluated from the linear dependence of the free energies on temperature.

*Keywords*: Silver ion complexes; Thiourea complexes; Enthalpy–entropy relationships; Non-aqueous solvents; Propan-2-one

## 1. Introduction

Previous contributions have been reported on thermodynamics of interactions between Ag(I)–thiourea or thiourea derivatives in aqueous solution and in several mono-hydroxyl hard solvents (alcohols) [1–5]. Owing to the occurrence of strong intermolecular hydrogen bond interactions, such solvents are structured in comparison with other hard solvents, such as propan-2-one, whose electronic structure does not allow hydrogen bonds and their liquid frameworks are not as rigid as the ones of hydrogen-bonded liquids.

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Because the nature and strength of solvent–solvent interactions affects solute–solvent interactions [6], they affect the chemical equilibria by multifaceted actions which are at the same time cooperative and competitive [7–10].

In the framework of systematic investigations on the role of alkyl substituents and the solvent medium on complex formation equilibria, in this contribution, potentiometric investigations on complex formation between Ag(I) and thiocarbonyl thiourea derivative ligands in propan-2-one are reported.

## 2. Experimental

### 2.1. *Chemicals*

Purity grade reagents from Fluka (purity grade >99%). Ag(I) solutions in propan-2-one prepared by successive dilutions from standard $10^{-2}$ M silver nitrate solution in the same solvent.

Ligands were recrystallized from saturated solutions in propan-2-one by slow-cooling in a refrigerator and were washed with the solvent, and the residual amount of solvent was removed under vacuum at 30 °C. Solutions ($10^{-2}$ M) were prepared by direct weighing.

Propan-2-one with water content <0.1% was periodically checked by KF titration.

### 2.2. *Apparatus*

Amel model 333 potentiometer (detection limit: 1 mV)

Silver electrodes were prepared by silver wire coil from Sigma Aldrich (purity grade >99%). At the investigated temperatures, the measuring cell was amply tested for thermodynamic reversibility, reproducibility, and speed of response by measuring the dependence of $\Delta E$ on $\ln[\mathrm{AgNO_3}]_{\mathrm{tot}}$ (tot: total concentration; $[\mathrm{AgNO_3}]_{\mathrm{tot}} = 5 \times 10^{-5}\mathrm{M}{-}5 \times 10^{-2}$ M) in the absence of ligands and any other interfering material. Nernst responses have been found with constant experimental sensitivities $\mathrm{d}E/\mathrm{d}(\ln[\mathrm{AgNO_3}]_{\mathrm{tot}})$ ($T = \mathrm{const.}$) within ±2–3% of the theoretical Nernst values at each investigated temperature.

### 2.3. *Procedure and calculations*

Silver nitrate solutions were titrated with ligand solutions in a thermostated room, and the potentiometric curves were electronically recorded.

In solution, silver nitrate simultaneously reacts with thiocarbonyl compounds producing both soluble colorless silver complexes and readily blackening colloidal insoluble material. In order to obtain colorless and over time very stable homogeneous solutions with total absence of precipitate, it is sufficient to enhance complex formation by slowly adding, under continuous stirring, Ag(I) solutions to solutions containing excess ligand, but not the vice versa. As a consequence, the solutions were prepared according to steps I°–III°:

I°: drawing the volume of solvent ($V_{\mathrm{solvent}}$);

II°: adding the minimum amount of ligand solution ($V_{\mathrm{titrant}}$) for complexing the Ag(I) solution which will be added subsequently;

III°: add the Ag(I) solution ($V_{\mathrm{AgNO3}}$) drop by drop while stirring.

It can be calculated $V_{tot} = V_{solvent} + V_{titrant} + V_{AgNO3}$. In this work, $V_{solvent} + V_{AgNO3} = 5$ mL and $V_{tot} = 5$ mL + $V_{titrant}$; $V_{tot}$ mL of complexed Ag(I) solutions was titrated with solution of the same ligand. The ligand, added before starting the titration, was taken into account in the calculations.

Investigated concentrations are as follows: $[\mathrm{Ag(I)}]_{tot} = 1 \times 10^{-5}$, $2 \times 10^{-5}$, $2.5 \times 10^{-5}$, $3 \times 10^{-5}$ and $4 \times 10^{-5}$ M; $[L]_{tot} = 5 \times 10^{-4}$ M$-5 \times 10^{-3}$ M; ligand to metal ion ratios from 12.5 to 500.

For each titration, the set of experimental data $\{\Delta E_{(i)}, [L]_{(i)tot}, [\mathrm{Ag(I)}]_{tot}\}$ was processed by means of an "ad hoc" devised nonlinear least squares algorithm, developed and implemented by the author. In output, $N_{max}$ (maximum coordination number), the best set of $\ln\beta_n$ ($n = 1 - N_{max}$; $\beta_n$ = stability constant for the overall complexing reaction $\mathrm{Ag(I)} + n\,L = \mathrm{Ag}L_n$ as mol$^{-n}$ dm$^{3n}$), the free (solvated) ligand concentrations $[L]_{free,}$ and the Ag(I)/Ag standard potential for the cell in scheme 1, which best describes the titration curves are given. The goodness of fit is checked by evaluating the distribution of the residuals and comparing the standard Ag(I)/Ag potential deduced from the titration curves with the values directly obtained from the Nernst dependence of $\Delta E$ on $\ln[\mathrm{AgNO_3}]_{tot}$.

The original experimental data, information about the algorithm, listing, and calculations can be obtained free of charge on request from the author.

## 3. Results and discussion

In order to properly describe the experimental data, the polynomial formation function $\Sigma_n \beta_n [L]^n_{free}$ must be composed at least by four subsequent terms with $n = 0$, 1, 2, and 3, which correspond to the presence of the successive complexes Ag$L$, Ag$L_2$, and Ag$L_3$ in the solution, except for the $\mathrm{AgNO_3}$–$\mathrm{Ph_2Tu}$ solution. For this system, it is sufficient to impose the analytically meaningful presence of the two complexes $\mathrm{Ag(Ph_2Tu)}$ and $\mathrm{Ag(Ph_3Tu)_2}$. The best values of $\ln\beta_n$ and the linearly deducible thermodynamic parameters $\Delta G_n$, $\Delta H_n$, and $\Delta S_n$ at 25 °C for the overall complex formation equilibria $\mathrm{Ag(I)} + n\ L = \mathrm{Ag}L_n$ are reported in table 1. The thermodynamic parameters $\ln K_{(n,n\text{-}1)} = \ln\beta_n - \ln\beta_{n-1}$, $\Delta G_{(n,n-1)} = \Delta G_n - \Delta G_{n-1}$, $\Delta H_{(n,n-1)} = \Delta H_n - \Delta H_{n-1}$, and $\Delta S_{(n,n-1)} = \Delta S_n - \Delta S_{n-1}$ for the stepwise formation $\mathrm{Ag}L_{n-1} + L = \mathrm{Ag}L_n$ are reported in table 2.

### 3.1. *Enthalpy–entropy relationships*

The thermodynamic parameters $\Delta G_n$, $\Delta H_n$, and $\Delta S_n$ for the overall equilibria are connected with the related stepwise $\Delta G_{(n,n-1)}$, $\Delta H_{(n,n-1)}$, and $\Delta S_{(n,n-1)}$ by the indexed summation ($\Delta X_n = \Sigma_n \Delta X_{(n,n-1)}$, $X = G, H,$ or $S$). Being free energies, enthalpies, and entropies are mutually related by the linear Gibbs–Helmholtz equation, on the occurrence of linear enthalpy–entropy relationships $\Delta H = \Delta H_{res} + \tau\ \Delta S$ for both the overall and stepwise complex equilibria; these relationships must be parallel. The experimental evidence shows this is the actual case (figure 1). For the overall complex formation series, $\mathrm{Ag(I)} + n\ L\mathrm{(i)} = \mathrm{Ag}L\mathrm{(i)}_n$: $\Delta H_{res} = -70 \pm 5$; $\tau = 0.24 \pm 0.02$; $T_{iso} = 241$ K; Corr. Coeff. = 0.889. For the stepwise complex formation reaction series, $\mathrm{Ag}L\mathrm{(i)}_{n-1} + L\mathrm{(i)} = \mathrm{Ag}L\mathrm{(i)}_n$: $\Delta H_{res} = -27 \pm 6$; $\tau = 0.26 \pm 0.04$: $T_{iso} = 261$ $K$; Corr. Coeff.: 0.910.

The angular coefficients $\tau$ of the compensative $\Delta H - \Delta S$ relationships are contained within the experimental error and can be interpreted as a single value pointing to single

Table 1. Stability constants $\ln\beta_n$ ($\beta_n$ as $dm^{3n}$ $mol^{-n}$) at different temperatures, free energy, enthalpy, and entropy changes at $t = 25$ °C (as kJ $mol^{-1}$, kJ $mol^{-1}$, and Joule $mol^{-1}$ $T^{-1}$, respectively) for the overall complex formation reactions $Ag(I) + n\ L = AgL_n$ and self-determined ionic medium (no background electrolyte added; ionic strength determined by the $AgNO_3$ concentration) in propan-2-one. The data at $t = 0-20$ °C are experimentally deduced. The data at $t = 25$ °C have been calculated from the (linear) dependence of free energy on $T$.

| | | $t = 0$ °C | $t = 5$ °C | $t = 10$ °C | $t = 15$ °C | $t = 20$ °C | $t = 25$ °C | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Ligand | $n$ | $\ln\beta_n$ | $\ln\beta_n$ | $\ln\beta_n$ | $\ln\beta_n$ | $\ln\beta_n$ | $\ln\beta_n$ | $\Delta G$ | $\Delta H$ | $\Delta S$ |
| Tu | 1 | – | 27.1 ± 0.6 | 25.8 ± 2.1 | 23.8 ± 0.2 | 23.2 ± 0.7 | 21.8 | 54.2 | −177 ± 21 | −412 ± 74 |
| | 2 | 37.1 ± 0.6 | 37.7 ± 0.6 | 35.9 ± 0. | 35.2 ± 0.4 | 34.5 ± 0.2 | 34.6 | 85.9 | −88 ± 41 | −7 ± 147 |
| | 3 | 44.8 ± 0.3 | 45.4 ± 0.4 | 45.8 ± 0.1 | 42.8 ± 0.3 | 42.2 ± 0.2 | 42.9 | 106.3 | −86 ± 57 | +68 ± 201 |
| Ta | 1 | 22.8 ± 0.7 | 20.9 ± 0.2 | 20.9 ± 0.9 | 22.3 ± 1.2 | 21.9 ± 0.8 | 22.8 | 56.5 | +21 ± 65 | +260 ± 236 |
| | 2 | 32.1 ± 0.7 | 30.8 ± 0.9 | 30.8 ± 0.4 | 30.2 ± 1 | 30.8 ± 0.6 | 30.7 | 76.1 | −34 ± 27 | +143 ± 96 |
| | 3 | 38.8 ± 0. | 37.4 ± 0.5 | 36.0 ± 0.3 | 38.5 ± 1.2 | – | 38.9 | 96.5 | +32 ± 25 | +431 ± 45 |
| MeTu | 1 | 23.2 ± 0.8 | 23.2 ± 0.7 | 23.3 ± 0.4 | 21.8 ± 0.6 | 23 ± 0.2 | 22.9 | 56.9 | −17 ± 22 | +134 ± 8 |
| | 2 | 35.7 ± 0.4 | 35.3 ± 0.2 | 34.3 ± 0.8 | 34.2 ± 0.4 | 34.4 ± 0.7 | 36.6 | 90.9 | +31 ± 46 | +405 ± 165 |
| | 3 | 43. ± 0.3 | 40.1 ± 0.7 | 42.3 ± 0.2 | 41.6 ± 0.6 | 41.6 ± 0.1 | 42.2 | 104.7 | −51 ± 42 | +180 ± 150 |
| EtTu | 1 | 25.0 ± 0.7 | 25.6 ± 1.4 | 25.9 ± 1 | 23.9 ± 0.8 | 24.6 ± 1.3 | 28.2 | 70.1 | −30 ± 30 | +134 ± 106 |
| | 2 | 36.3 ± 0.3 | 36.5 ± 1.1 | 35.7 ± 1.2 | 34.6 ± 0.3 | 34.4 ± 1.1 | 34.8 | 86.2 | −60 ± 31 | +88 ± 110 |
| | 3 | 44.6 ± 0.4 | 42.3 ± 0.6 | 43.5 ± 0.8 | 41.9 ± 0.5 | 42.4 ± 1.3 | 42.1 | 104.5 | −81 ± 38 | +79 ± 134 |
| Et$_2$Tu | 1 | 24.7 ± 1 | 23.5 ± 0.4 | 22.8 ± 0.4 | 21.1 ± 0.7 | 20.9 ± 0.7 | 18.5 | 45.8 | −124 ± 15 | −249 ± 54 |
| | 2 | 36.3 ± 0.5 | 34.5 ± 1 | 39.8 ± 0.5 | 31.9 ± 0.5 | 31.4 ± 0.2 | 30.7 | 76.1 | −150 ± 11 | −248 ± 112 |
| | 3 | 42.5 ± 1.7 | 42.9 ± 1 | 40.8 ± 0.3 | 40.4 ± 0.5 | 38.1 ± 0.4 | 40.6 | 100.8 | −99 ± 22 | +6 ± 257 |
| PhTu | 1 | 21.5 ± 0.9 | 23.2 ± 0.5 | 24.4 ± 0.9 | 20.9 ± 0.7 | 20.6 ± 0.2 | 21.6 | 53.5 | −32 ± 72 | +74 ± 250 |
| | 2 | 34.7 ± 0.4 | 34.8 ± 0.2 | 33.9 ± 1.3 | 32.9 ± 0.5 | 31.4 ± 0.5 | 31.7 | 78.5 | −100 ± 43 | −2 ± 153 |
| | 3 | 42.3 ± 0.4 | 46.7 ± 0.1 | 41.5 ± 0.2 | 40.2 ± 0.2 | 39 ± 0.4 | 39.6 | 98.2 | −89 ± 45 | +31 ± 161 |
| Ph$_2$Tu | 1 | 20.9 ± 0.6 | 20.1 ± 0.4 | 20.5 ± 0.7 | 18.4 ± 0.6 | 19.8 ± 0.8 | 19.8 | 49.1 | −25 ± 26 | +81 ± 93 |
| | 2 | 31.6 ± 1 | 32.2 ± 0.3 | 33.6 ± 1.5 | 30.3 ± 0.6 | 29.9 ± 1.4 | 31.9 | 79.2 | −33 ± 76 | +155 ± 270 |
| | 3 | 39.3 ± 1.0 | 38.5 ± 0.3 | – | – | – | – | – | – | – |
| TbAn | 1 | 16.2 ± 0.1 | 16.1 ± 0.4 | 16.0 ± 0.8 | 14.1 ± 0.4 | 15.4 ± 0.1 | 14.7 | 36.4 | −43 ± 26 | −22 ± 90 |
| | 2 | 25.7 ± 0.9 | 25.7 ± 0.4 | 24.3 ± 0.6 | 23.8 ± 0.1 | 22.1 ± 0.3 | 22.2 | 55.2 | −141 ± 38 | −187 ± 33 |
| | 3 | 31.5 ± 0.7 | 35.0 ± 1.1 | 33.0 ± 4 | 29.1 ± 0.4 | 30.5 ± 0.2 | 31.7 | 78.7 | −28 ± 48 | +170 ± 17 |

Table 2. Stability constants $\ln K_{n,n-1)}$ ($K_n$ as dm$^3$ mol$^{-1}$), standard free energy $\Delta G_{(n,n-1)}$, enthalpy $\Delta H_{(n,n-1)}$, and entropy $\Delta S_{(n,n-1)}$ changes (as kJ mol$^{-1}$, kJ mol$^{-1}$, and Joule mol $T^{-1}$, respectively) for the stepwise complex formation reactions $AgL_{(n-1)} + L = AgL_n$ at $t = 25$ °C and self-determined ionic medium (no background electrolyte added; ionic strength determined by the $AgNO_3$ concentration) in propan-2-one at $t = 25$ °C calculated from the data in table 1.

| Ligand | *n* | $\ln K_{(n,n-1)}$ | $-\Delta G_{(n,n-1)}$ | $\Delta H_{(n,n-1)}$ | $\Delta S_{(n,n-1)}$ |
|---|---|---|---|---|---|
| Tu | 1 | 21.8 | 54.16 | −177 | −412 |
| | 2 | 12.8 | 32.71 | +89 | +409 |
| | 3 | 8.3 | 20.0 | +2 | +75 |
| | 1 | 22.8 | 56.5 | +21 | +260 |
| Ta | 2 | 7.9 | 19.6 | −55 | −117 |
| | 3 | 8.2 | 20.4 | +66 | +288 |
| | 1 | 22.9 | 56.9 | −17 | +131 |
| MeTu | 2 | 13.7 | 34.0 | +40 | +271 |
| | 3 | 5.4 | 13.8 | −82 | −229 |
| | 1 | 28.2 | 70 | −30 | +134 |
| EtTu | 2 | 6.6 | 16.1 | −30 | −46 |
| | 3 | 7.6 | 18.1 | −21 | −5 |
| | 1 | 18.5 | 45.8 | −124 | −249 |
| E$_{t2}$Tu | 2 | 12.9 | 30.2 | −26 | +1 |
| | 3 | 9.9 | 24.7 | +57 | 254 |
| | 1 | 21.5 | 53.5 | −32 | +74 |
| PhTu | 2 | 10.8 | 25 | −68 | −146 |
| | 3 | 8 | 19.7 | +11 | +103 |
| | 1 | 19.8 | 49.1 | −25 | +81 |
| $Ph_2Tu$ | 2 | 12.1 | 30.1 | −8 | +74 |
| | 1 | 14.7 | 36.4 | −43 | −22 |
| TbAn | 2 | 7.6 | 18.8 | −68 | −165 |
| | 3 | 9.5 | 23.5 | +83 | +357 |

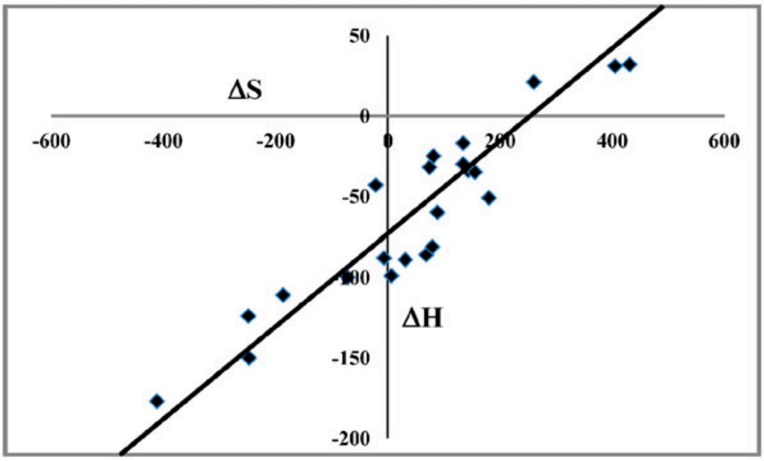

Figure 1. $\Delta H$ *vs*. $\Delta S$ linear compensative relationship $\Delta H = \Delta H_{res} + \tau\Delta S$ for the overall complex formation reaction series Ag(I) + $n\ L(i) = AgL(i)_n$ ($n$ = 1–3; $L(i)$ : thiourea derivative thiocarbonyl ligands; $i$ = variable).

isoequilibrium temperature within the range from −39 to 19 °C. Hence, the isoequilibrium temperature is experimentally accessible for the liquid range of the solvent from −95.4 °C (melting point of propan-2-one) to 56.2 °C (boiling point). Having unique isoequilibrium temperature, the reactions form a homologous series characterized by a single "energetic mechanism" [11], which allows the reactions to be organized according to well-defined ranks. At the isoequilibrium temperature, the reactions became free energy undiscriminated for having the same mutual substratum-to-ligand affinity, and the $\Delta G$ *versus* $T$ relationships are a sheaf of functions constrained at the (single) pole ($\Delta G_{\mathrm{iso}}, T_{\mathrm{iso}}$). On the occurrence of linear dependence of $\Delta G$ on $T$ (or within enough narrow temperature range in the neighborhood of $T_{\mathrm{iso}}$), the affinity divergences between equilibria **a** and **b** are proportionally related to $T - T_{\mathrm{iso}}$, and the isoequilibrium temperature represents the inversion point for the affinity sequence ($\Delta G_{\mathbf{a}} - \Delta G_{\mathbf{b}} = \alpha_{(\mathbf{a},\mathbf{b})} \ (T - T_{\mathrm{iso}})$ where $\alpha_{(\mathbf{a},\mathbf{b})}$ is the entropy difference between the equilibria. This does not mean that the reactions are entropy-driven for entropy and enthalpy changes are mutually connected). From the $\tau$ values, it can be calculated $T_{\mathrm{iso}} = 245 \pm 5$ K ($t_{\mathrm{iso}} = -28.5 \pm 5$ °C) as weighted mean of the isoequilibrium temperatures (weight $= \sigma(\tau)^{-2}$) where from the following $\Delta G_{\mathrm{iso}}$ are estimated:

(1) Homologous series $\mathrm{Ag(I)} + nL(\mathrm{i}) = \mathrm{Ag}L(\mathrm{i})_{\mathrm{n}}$ ($n = 1$–$3$; $i$ = variable)

$n = 1$, $\Delta G_{\mathrm{iso}} = -53.5 \pm 12$ kJ mol$^{-1}$;
$n = 2$, $\Delta G_{\mathrm{iso}} = -75.2 \pm 11$ kJ mol$^{-1}$;
$n = 3$, $\Delta G_{\mathrm{iso}} = -91.3 \pm 12$ kJ mol$^{-1}$.

(2) Homologous series $\mathrm{Ag}L(\mathrm{i})_{\mathrm{n-1}} + L(\mathrm{i}) = \mathrm{Ag}L(\mathrm{i})_{\mathrm{n}}$ ($n = 1$–$3$; $i$ = variable)

$n = 1$, $\Delta G_{(1,0)\mathrm{iso}} = -53.5 \pm 12$ kJ mol$^{-1}$;
$n = 2$, $\Delta G_{(2,1)\mathrm{iso}} = -24.1 \pm 16$ kJ mol$^{-1}$;
$n = 3$, $\Delta G_{(3,2,)\mathrm{iso}} = -12.2 \pm 18$ kJ mol$^{-1}$.

The two sets of isoequilibrium free energies are self-consistent within the experimental error.

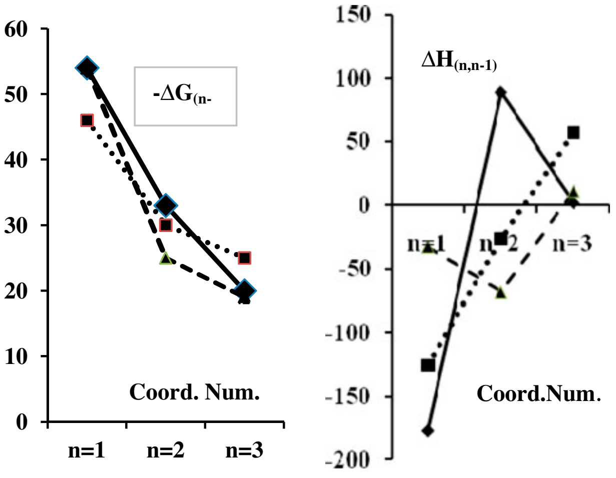

Figure 2. Free energy (left side diagram) and enthalpy change patterns (right side diagram) with respect to coordination number for the stepwise complex formation reactions $\mathrm{Ag}L_{(\mathrm{n}-1)} + L = \mathrm{Ag}L_{\mathrm{n}}$ with selected ligands. The entropy changes show the same pattern of the enthalpy change. Solid line: Tu; dotted line: $\mathrm{Et_2Tu}$; dashed line: PhTu.

Measuring cell:

| | | | | |
|---|---|---|---|---|
| | $[AgNO_3]_{tot}$=const. | $LiNO_3$ | AgCl | |
| | [L]=Var. (titrant) | sat. salt bridge | in sat. KCl | |
| Ag | propan-2-one | in propan-2-one | aqueous | Ag |
| | Inz.Vol.$V_0$=5 ml | | solution | |
| | Measur. half cell | | Ref. half cell | |

Scheme 1.

### 3.2. *Free energy, enthalpy, and entropy data*

Regardless of the alkyl-substitution, the mutual substratum-to-ligand affinities for the stepwise reactions follow the general sequence $\Delta G_{(1,0)} << \Delta G_{(2,1)} \le \Delta G_{(3,2)}$ (figure 2). As the free energies sensitively depend on the experimental conditions, the internal quantitative relations change with temperature even though related to stepwise reactions, and so also it can be for the rank in case of occurrence of experimental accessible isoequilibrium conditions.

In the actual case of a unique isoequilibrium temperature, independent from series and substituents (figure 1), on $T = T_{iso}$, the (univocal) $\Delta G_{iso}$ sequences can be supposed to be joined to the nature of the systems (Ag(I)–thiourea or thiocarbonyl thiourea-related ligands -propan-2-one). Greater the difference $T - T_{so}$, greater is the influence of the alkyl substituents on the stepwise equilibria. At $t = 25$ °C ($T > T_{iso}$), the alkyl substituents tend to lower the substratum-to-ligand affinities. At $T = T_{iso}$, they have no effect. At $T < T_{iso}$, the trend is reversed.

On increasing the thermodynamic stabilities of the reacting substrata, the affinities ($\Delta G_{(n.n-1)}$, $n = 1$–3) are confined within progressively narrower ranges. For the first complexing reactions $Ag(I) + L(i) = AgL(i)$ ($i$ = variable), the amplitude of the affinity range is $\approx$40 kJ mol$^{-1}$ from $\approx -75$ to $\approx -30$ kJ mol$^{-1}$; for the 2nd stepwise complexing reactions $AgL(i) + L(i) = AgL(i)_2$, $\approx$20 kJ mol$^{-1}$ from $\approx -35$ to $\approx -15$ kJ mol$^{-1}$; and for the 3rd stepwise complexing reactions $AgL(i)_2 + L(i) = AgL(i)_3$, $\approx$12.5 kJ mol$^{-1}$ from $\approx -25$ to $\approx -12.5$ kJ mol$^{-1}$. In general, the substrata tend to undergo minor changes, greater are their thermodynamic stabilities. This statement is qualitatively invariant with temperature, but the free energy intervals are quantitatively reduced on approaching the isoequilibrium conditions.

In the framework of compensative interplay (figure 1), enthalpy and entropy changes are much more affected by the alkyl substituents than the corresponding affinities (figure 2). In spite of their apparent irregular (but not casual) variability of $\Delta H$, promptly compensated by the corresponding $\Delta S$, a sort of regularity can be easily disclosed, which ensures an internal structure in the $\Delta H$ ($\Delta S$) set of data.

The Ag(I) complex formation reactions with thioureas in propan-2-one are structure making reactions as they are exothermic and entropy disfavored (for the exceptions, the reader can refer to the tables or to the figures). In spite of the large and apparently chaotic variability of the enthalpy (entropy), the internal structure emerges by analyzing the set of the stepwise $\Delta H$ ($\Delta S$) data. By comparing the relationship between two subsequent stepwise enthalpy changes, $\Delta H_{(1,0)}$ and $\Delta H_{(2,1)}$, with the relationship between the following $\Delta H_{(2,1)}$ and $\Delta H_{(3,2)}$ for the stepwise reactions with the same ligand, it can be concluded that the relationship between $\Delta H_{(1,0)}$ and $\Delta H_{(2,1)}$ and relationship between the subsequent $\Delta H_{(2,1)}$ and $\Delta H_{(3,2)}$ are reverted or tend to be reverted. The same holds for the entropy changes.

## 4. Remarks

In aqueous solution, silver ion behaves differently when reacting with ligands having hard or soft donors [12,13]. With soft donor ligands, the complexing reactions lead to stepwise formation of four-coordinate complexes with stepwise free energy sequence $\Delta G_{(1,0)} << \Delta G_{(2,1)} \approx \Delta G_{(3.2)} < \Delta G_{(4,3)} < 0$, with the formation curves (average coordination number *versus* $[L]_{\mathrm{free//tot}}$) having large plateau at $n = 1$ and inflection at $n = 3$. Previous investigations on Ag(I)–thiourea complexes in aqueous solution show formation of four-coordinate $\mathrm{AgTu}_4$ [12]. Owing to the analogy among the structure of thiourea and thiocarbonyl thiourea-related ligands, it is legitimate to foresee $N_{\max} = 4$ as maximum coordination number for the systems investigated in the present work, and four-coordinates $\mathrm{Ag}L_4$ has not been detected as their presence is below the detection limit in the investigated ligand concentration range.

The actual considerations on the behavior of the free energy changes strengthen the already formulated assertion [14,15] about the influence of coordinated ligands on the coordinating abilities toward further entering group(s) in non-exhaustively coordinated substrata; the greater the thermodynamic stability of the reacting substratum, the lower is its tendency to bind further ligand(s). The narrowing of the free energy ranges which contain the affinities of reactions $\mathrm{Ag}L_{\mathrm{n}-1} + L = \mathrm{Ag}L_{\mathrm{n}}$, in dependence on stabilities of the reacting substrata confirms, though indirectly, the above sentence.

The mostly negative enthalpy(entropy) changes (only few exceptions occur) disclose that the investigated systems gain geometrical order and/or stiffness, and the Ag(I)–thiourea complex formation reactions are structure-making reactions. Whatever the final status of the systems resulting from the formation reactions, the stepwise $\Delta H$ ($\Delta S$) alternating changes demonstrate the alternating structural changes which correspond to the successive coordination of single incoming ligands.

Compared to the previously found isoequilibrium relationships in more structured protic solvents [1–4], clearly minor, all the same positive enthalpy-entropy susceptivity ($\tau = \mathrm{d}H/\mathrm{d}S$) is found in propan-2-one solutions. It is legitimate to suppose that solvent–solvent interactions have repercussions on solute–solvent interactions and in general on the whole system behavior; in less-structured solvents the reorganization of the solutions as consequence of any process must involve lower energy and probably greater entropy changes. Hence, to equal $\Delta S$ values correspond different $\Delta H$ values increasing with the strength (structuring ability) of the solvent–solvent interactions. This behavior can be expressed in tautological way by exchanging the entropy with the enthalpy; to equal values of enthalpy changes correspond different decreasing entropy changes with the strength of solvent–solvent interactions. Such an interpretation ascribes (at least) part of the $\Delta H$–$\Delta S$ interplay to the changes in the solvation status between reagents and products and indicates a sort of dependence of the isoequilibrium temperatures on physical structural parameters of the solvent medium.

## Disclosure statement

No potential conflict of interest was reported by the author.

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