

## Research Article

# Complex Formation Equilibria between Ag(I) and Thioureas in Propan-2-ol

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Received 25 June 2013; Accepted 8 September 2013

Academic Editors: M. S. Masoud and J. Zhang

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The complex formation equilibria between Ag(I) and thiourea (Tu), N-methyl-Thiourea (MeTu), N,N'-dimethyl-Thiourea (Me<sub>2</sub>Tu), N,N,N',N'-Tetramethyl-Thiourea (Me<sub>4</sub>Tu), N-ethyl-Thiourea (EtTu), N,N'-diethyl-Thiourea (Et<sub>2</sub>Tu), and N,N'-Ethylene-Thiourea (EnTu) in propan-2-ol as solvent medium have been investigated by potentiometry within the temperature range 10°C–40°C and self-determined ionic medium by (AgNO<sub>3</sub>) concentration range  $6.36 \cdot 10^{-6}$ – $3.83 \cdot 10^{-5}$  m·dm<sup>-3</sup> (no background electrolyte added). The experimental results can be interpreted with the stepwise formation of tris-coordinated complexes AgL<sub>n</sub> ( $n = 1-3$ ; hereafter charge is omitted). The stability constants  $\log \beta_n$  and the standard thermodynamic changes in enthalpy ( $\Delta H_n^\circ$ ) and entropy ( $\Delta S_n^\circ$ ) for overall complex formation reactions  $\text{Ag(I)} + n\text{L} = \text{AgL}_n$  ( $n = 1-3$ ) have been evaluated. The reactions are exothermic in nature and entropy disfavored for all the investigated ligands. The standard enthalpy and entropy changes for the stepwise reactions  $\text{AgL}_{n-1} + \text{L} = \text{AgL}_n$  have been evaluated by difference  $\Delta(\Delta H_n^\circ) = \Delta H_n^\circ - \Delta H_{n-1}^\circ$  and  $\Delta(\Delta S_n^\circ) = \Delta S_n^\circ - \Delta S_{n-1}^\circ$ . The stepwise enthalpy are mutually linearly related to the corresponding entropy changes with isoequilibrium temperatures  $T_{\text{iso}} = 285, 305, \text{ and } 363$  K for  $n = 1, 2, \text{ or } 3$  respectively.

## 1. Introduction

In homogeneous equilibria, the solvent medium operates simultaneously on both reactants and products and influences the chemical reactions with counteracting actions which originate from solute-solvent and solvent-solvent interactions. The quantitative balance of such interactions together with the solute-solute interactions determines the actual position of the chemical equilibrium [1–5].

Systematic investigations on single series of reactions but different solvents are of utmost importance for disclosing the role of both the solvents and the various elements of the series on the metal-to-ligand interactions.

Thioureas and in general thiocarbonyl compounds are soft ligands which in hard solvents coordinate to soft metal ions via sulfur atom(s) [6, 7]. They show relevant chemical affinities towards Ag(I) forming in hydroxyl solvents complexes with high thermodynamic stability ([8, 9] and cited references).

In hydrogen donor solvents, thioureas undergo simultaneous solvation both at the sulfur atom via the acceptor atom(s) of the solvent and, when not exhaustively N-alkylated, to the hydrogen atoms via the donor atom(s) of the solvent.

In hard solvents, in comparison with other metal ions in their ordinary oxidation states, silver ion has remarkable oxidizing properties which suggest that Ag(I) undergoes no strong solvation in such solvents.

The coordination of thiocarbonyl compounds to soft metal ions occurs via sulphur atom(s). The coordination to Ag(I) involves desolvation of both the acceptor Ag(I) and the donor atoms of the ligand and the reinforcement the bond between the hydrogen atoms of the amide groups of the coordinated ligand(s) and the oxygen atom of the solvating solvent [8, 9].

In this contribution, the results of investigations on thermodynamics of complex formation equilibria between Ag(I) and thiourea or N-alkyl-substituted thioureas in propan-2-ol

are reported. The investigation has been performed by potentiometry at different temperatures ( $T = 283.16\text{--}313.16\text{ K}$ ). Standard free energy changes ( $\Delta G^\circ$ ) for the complex formation reactions have been deduced from the stability constants, while standard enthalpy and entropy changes,  $\Delta H^\circ$  and  $\Delta S^\circ$ , from the dependence of  $\Delta G^\circ$  on temperature.

## 2. Experimental

**2.1. Reagents.** The ligands were commercial products (Fluka; purity grade > 98%) recrystallized from acetone and vacuum dried over  $\text{P}_2\text{O}_5$ . The standard ligand solutions, in propan-2-ol, were prepared by direct weighing. Ag(I) solutions in propan-2-ol were prepared by successive dilutions from  $\text{AgNO}_3$  (Fluka; ACS reagent, purity > 99%) vacuum dried over  $\text{P}_2\text{O}_5$ . Propan-2-ol (Fluka; water content < 0.1% determined by KF), used without further purification.

The water content of the reagent solutions and solvent was periodically checked by KF method.

**2.2. Measurements.** Potentiometric measurements have been carried out in thermostated cell. The cell is reproduced in Scheme 1.

Silver electrodes have been made by silver wire coils from Sigma-Aldrich (purity > 99.9%). The electromotive force has been measured by an AMEL mod 333 apparatus (accuracy 1 mV). Stability, speed of response, thermodynamic reversibility, and reproducibility of the potentiometric apparatus have been experimentally checked by measuring the experimental relationships  $\Delta E$  versus  $\ln [\text{AgNO}_3]_{\text{tot}}$  in absence of ligand. The system resulted very stable, the measures very reproducible, and the response immediate. The Nernst slopes, always found within  $\pm 1\%$  of the theoretical values, demonstrate the reversibility of the system.

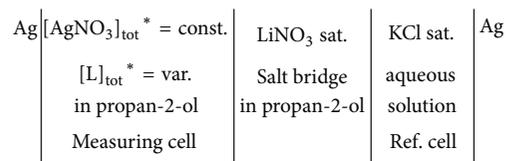
**2.3. Procedure.** Ag(I) solutions (5 mL) in propan-2-ol containing constant amounts of  $\text{AgNO}_3$  (the measuring cell) have been titrated with ligand solutions  $10^{-2}\text{ m}\cdot\text{dm}^{-3}$ . At every temperature, five different  $\text{AgNO}_3$  solutions with different initial total concentration of silver nitrate ( $[\text{AgNO}_3]_{\text{tot}} = 5 \times 10^{-6}, 10 \times 10^{-6}, 15 \times 10^{-6}, 20 \times 10^{-6}$  and  $30 \times 10^{-6}\text{ m}\cdot\text{dm}^{-3}$ , resp.) have been titrated.

The ligand total concentration in the titrated solution ranges from  $[\text{L}]_{\text{tot}} = 1.33 \times 10^{-4}\text{ m}\cdot\text{dm}^3$  to  $1.8 \times 10^{-3}\text{ m}\cdot\text{dm}^3$  ( $[\text{L}]_{\text{tot}}/[\text{Ag(I)}]_{\text{tot}} \gg 1$ ).

No supporting electrolyte has been added. The ionic strength of the solutions is self-determined by  $[\text{AgNO}_3]_{\text{tot}}$ .

In order to prepare stable and colorless solutions to be titrated with ligand, the initial solution has been prepared by adding the suitable amount of  $\text{AgNO}_3$  solution to solution containing the ligand in concentration  $1.33 \times 10^{-4}\text{ m}\cdot\text{dm}^{-3}$  under continuous stirring.

For every Ag(I)—Ligand system, the experimental results consist of about 4200 experimental points uniformly distributed over eight different temperatures. The original primary experimental data can be obtained on request from the author(s) free of charge.



\* Total molar concentration of  $\text{AgNO}_3$  or L = ligand.

SCHEME 1

**2.4. Calculations.** The Nernst equation  $\Delta E = \Delta E_0 + RT/(nF) \ln ([\text{Ag(I)}]_{\text{tot}}/\sum_n \beta_n [\text{L}]_{\text{free}}^n) - [\text{L}]_{\text{free}}$ : molar concentration of solvated (free) ligand—describes the response of the electrode system to the variable composition of the investigated solution. For each single titration, the experimental set of data  $\{\Delta E_{\text{exp}}, [\text{Ag(I)}]_{\text{tot}}, [\text{L}]_{\text{tot}}\}$  has been processed until the sum of the squared residuals  $U = \sum_i (\Delta E_{\text{exp}} - \Delta E_{\text{cal}})^2$  has been minimized with respect to  $\Delta E_0$  and  $\{\ln \beta_n\}$  by using an original routine “ad hoc” conceived, written, and implemented by one of the authors. Details about the algorithm, the listing, calculations, and so on can be freely obtained from the authors.

As to the composition of the investigated systems, the lowest number of successive  $\text{AgL}_n$  complexes, which adequately describe the set of experimental data, has been assumed.

The calculated  $\Delta E_0$  values at each temperature from the titration curves were always consistent with the values experimentally deduced from  $\Delta E$  versus  $\ln [\text{Ag(I)}]_{\text{tot}}$  relationships in absence of ligand.

## 3. Results and Discussion

The experimental data for every system at every temperature can be described by the presence in solution of three stepwisely formed  $\text{AgL}_n$  ( $n = 1\text{--}3$ ) complexes. The estimated residual ( $\Delta E_{\text{exp}} - \Delta E_{\text{cal}}$ ) values were in agreement with the estimated experimental error ( $\approx \pm 2\text{ mV}$ ) and symmetrically distributed around the calculated values.

The overall stability constants ( $\log_{10} \beta_n$ ) for the complexing reactions  $\text{Ag(I)} + n\text{L} = \text{AgL}_n$ , as primary deduced directly from the experimental  $\{\Delta E_{\text{exp}}, [\text{L}]_{\text{tot}}\}$  data, are reported in Table 1. In Table 2, the most probable  $\text{Ag(I)} + n\text{L} = \text{AgL}_n$  values of thermodynamic parameters at  $25^\circ\text{C}$ , as deduced by linear regression from  $\{\Delta G^\circ, T\}$  data of Table 1, are reported. The predominance diagrams and the formation curves for both Ag(I)—thiourea and Ag(I)—substituted thioureas systems show large ligand concentration ranges with prevalence of the monocoordinated  $\text{AgL}$ . Both predominance diagrams and formation curves are not reported for they can be easily visualized by means of software available from the web or from the authors.

On increasing the coordination number of the reacting substratum the stepwise substratum-to-ligand affinities ( $\Delta(\Delta G^\circ)_n$  for the reaction  $\text{AgL}_{n-1} + \text{L} = \text{AgL}_n$ ) decrease especially between mono- and biscoordinated substrata (affinity sequence  $\Delta(\Delta G^\circ)_1 < \Delta(\Delta G^\circ)_2 < \Delta(\Delta G^\circ)_3$ ).

TABLE 1: Stability constants  $\log \beta_n$  ( $\beta_n$  as  $\text{m}^{-n} \cdot \text{dm}^{3n}$ ) and standard free energy changes  $\Delta G^\circ$  (as  $\text{kJ} \cdot \text{m}^{-1}$ ) at different temperatures and  $\log \beta_n$ , ionic strength self-determined by  $[\text{AgNO}_3] = 6.36 \times 10^{-6} - 3.83 \times 10^{-5} \text{ m} \cdot \text{dm}^{-3}$  for the overall complexing reactions  $\text{Ag}(\text{I}) + n\text{L} = \text{AgL}_n$ .

Ligand	$n$	$T = 283.2 \text{ K}$		$T = 288.2 \text{ K}$		$T = 293.2 \text{ K}$		$T = 298.2 \text{ K}$		$T = 303.2 \text{ K}$		$T = 308.2 \text{ K}$		$T = 313.2 \text{ K}$	
		$\log \beta_n$	$-\Delta G^\circ$												
Tu	1	10.6 ± 0.3	57.6	17.3 ± 0.5	61.0	9.8 ± 0.3	55.2	9.6 ± 0.1	54.9	9.7 ± 0.1	56.4	21.2 ± 0.6	54.5	20.7 ± 0.7	53.8
	2	14.7 ± 0.1	79.8	14.9 ± 0.2	84.9	14.4 ± 0.0	78.4	13.5 ± 0.1	77	13.5 ± 0.1	78.3	13.3 ± 0.0	77	12.5 ± 0.3	75.2
	3	17.3 ± 0.1	93.9	16.9 ± 0.3	96.5	16.5 ± 0.0	92.8	16.3 ± 0.0	92.9	15.8 ± 0.2	91.4	15.1 ± 0.1	89.3	15.3 ± 0.1	91.6
MeTu	1	10.6 ± 0.1	57.7	10.9 ± 0.3	58.9	9.8 ± 0.1	55.1	9.6 ± 0.4	55	9.3 ± 1.6	52.3	9.2 ± 0.3	54.4	8.1 ± 0.3	48.7
	2	14.8 ± 0.1	80.7	14.2 ± 0.0	81.4	13.6 ± 0.0	76.6	13.7 ± 0.2	78.1	13.3 ± 0.2	74.4	12.1 ± 0.0	75.7	12.3 ± 0.0	73.9
	3	17.4 ± 0.0	94.3	16.6 ± 0.2	94.7	16.4 ± 0.1	92.0	16.1 ± 0.2	91.9	15.5 ± 0.0	90	14.9 ± 0.2	88.1	14.0 ± 0.1	85.7
Me <sub>2</sub> Tu	1	10.7 ± 0.5	28.1	9 ± 0.3	51.4	8.6 ± 0.2	48.2	8.7 ± 0.2	49.9	8.6 ± 0.4	49.6	7.4 ± 0.5	43.6	7.6 ± 0.2	45.4
	2	14 ± 0.7	75.8	13.2 ± 0.0	75.7	12.7 ± 0.0	71.5	12.5 ± 0.0	71.1	12.5 ± 0.4	72.9	11.9 ± 0.0	74.3	11.6 ± 0.0	69.8
	3	17.0 ± 0.8	92.3	15.8 ± 0.0	90.1	15.3 ± 0.1	85.7	14.9 ± 0.0	84.5	35 ± 1.2	88.1	32.0 ± 0.5	82.1	31.8 ± 0.1	82.7
Me <sub>4</sub> Tu	1	7.6 ± 0.2	41.4	7.5 ± 0.8	42.9	6.1 ± 0.2	34.0	6.3 ± 0.0	36.1	5.9 ± 0.2	33.9	6 ± 0.3	5.5	5.4 ± 0.3	32.4
	2	11.6 ± 0.0	62.9	11.3 ± 0.1	64.4	10.6 ± 0.2	59.2	10.6 ± 0.1	60.2	12.7 ± 0.0	60.7	12.6 ± 0.0	59.5	9.8 ± 0.0	58.9
	3	14.5 ± 0.1	78.5	14.3 ± 0.0	81.6	13.6 ± 0.1	75.7	13.2 ± 0.0	85.4	12.3 ± 0.2	71.7	12.1 ± 0.3	71.5	12.0 ± 0.2	72.6
EtTu	1	10.4 ± 0.1	56.4	9.5 ± 0.0	58.9	9.5 ± 0.1	53.3	9.5 ± 0.0	54	9.2 ± 0.1	53.7	9 ± 0.2	53.1	9.6 ± 0.4	57.3
	2	14.9 ± 0.1	80.9	14.2 ± 0.1	80.8	14 ± 0.0	78.4	13.5 ± 0.1	77.3	13.2 ± 0.0	76.9	12.9 ± 0.1	76.2	12.9 ± 0.1	77.7
	3	17.9 ± 0.1	97	17 ± 0.1	96.8	16.5 ± 0.3	92.2	15.8 ± 0.2	91	15.7 ± 0.2	90.9	15.5 ± 0.1	91.2	15.3	91.8
Et <sub>2</sub> Tu	1	11.9 ± 0.1	61.2	10.6 ± 0.2	60.8	9.5 ± 0.1	53.5	9.3 ± 0.2	53.4	9.2 ± 0.1	53.1	9 ± 0.1	53.1	8.4 ± 0.3	50.5
	2	15.3 ± 0.1	83.1	14.7 ± 0.0	84.1	14.8 ± 0.0	77.5	13.6 ± 0.1	77.4	13.3 ± 0.1	77.5	14.7 ± 0.1	78.4	12.7 ± 0.1	76.4
	3	18.5 ± 0.2	100.2	17.7 ± 0.0	101.3	16.8 ± 0.0	94.5	16.4 ± 0.1	92.9	16.0 ± 0.0	93.4	15.9 ± 0.1	94	15.2 ± 0.1	91.1
EnTu	1	12.9 ± 0.3	69.7	12.1 ± 0.2	68.9	12.3 ± 0.3	68.9	11.0 ± 0.1	62.9	10.7 ± 0.1	62.5	11.1 ± 0.0	65.3	10.5 ± 0.1	63.4
	2	16.5 ± 0.1	89.3	15.6 ± 0.1	90.8	15.9 ± 0.1	89.3	15.2 ± 0.0	87.1	14.8 ± 0.0	86.4	14.6 ± 0.1	84.4	14.3 ± 0.1	85.6
	3	19.2 ± 0.1	110	18.4 ± 0.1	105	17.8 ± 0.2	98.4	17.1 ± 0.1	98	16.5 ± 0.2	96.1				

The alkyl substituents on the molecules of ligands influence the metal-to-ligand affinities differently in dependence on the coordination level of the complex substratum. In the formation of monocoordinates  $\text{AgL}$  complexes, the substitution of the hydrogen atom(s) of thiourea with alkyl group(s) lowers the ligand affinity toward  $\text{Ag}(\text{I})$  with the sole exception of Ethylene-thiourea. The standard free energies are dispersed within  $\approx 30 \text{ kJ} \cdot \text{m}^{-1}$  between  $\approx -65 \text{ kJ} \cdot \text{m}^{-1}$  for the reaction  $\text{Ag}(\text{I}) + \text{EnTu} = \text{AgEnTu}$  and  $\approx -36 \text{ kJ} \cdot \text{m}^{-1}$  for the reaction  $\text{Ag}(\text{I}) + \text{Me}_2\text{Tu} = \text{AgMe}_2\text{Tu}$  (affinity sequence  $\Delta(\Delta G^\circ)_1 < \Delta(\Delta G^\circ)_2 < \Delta(\Delta G^\circ)_3$ ). In the subsequent 2nd stepwise coordination reactions  $\text{AgL} + \text{L} = \text{AgL}_2$ , the influence operates in the opposite direction. The affinity range is reduced to  $\approx 7 \text{ kJ} \cdot \text{mL}^{-1}$  from  $\approx -28 \text{ kJ} \cdot \text{m}^{-1}$  for the reaction  $\text{AgMe}_2\text{Tu} + \text{Me}_2\text{Tu} = \text{Ag}(\text{Me}_2\text{Tu})_2$  and  $\approx 21 \text{ kJ} \cdot \text{m}^{-1}$  for the reaction  $\text{AgMeTu} + \text{MeTu} = \text{Ag}(\text{MeTu})_2$ .

In the coordination of the third ligand  $\text{AgL}_2 + \text{L} = \text{AgL}_3$ , the affinity range is comparable with the previous one.

The overall complexing reactions are simultaneously exothermal and entropy disfavored. The alkyl substituents influence sensitively the enthalpy and the entropy changes affecting both the parameters in parallel way: positive (negative) changes in  $\Delta H^\circ$  values correspond to positive (negative) changes in  $\Delta S^\circ$  values.

In the stepwise complexing reactions the influence of the alkyl-substituents manifests in reversed order in the subsequent coordination levels of the reacting substratum.

For the reaction series  $\text{Ag}(\text{I}) + \text{L}_{(i)} = \text{AgL}_{(i)}$  ( $\text{L}_{(i)}$  = variable) the sequence of stepwise enthalpy changes  $\Delta(\Delta H^\circ)_n = \Delta H_n^\circ - \Delta H_{n-1}^\circ$  is  $\Delta(\Delta H^\circ)_{1\text{Me}_2\text{Tu}} \sim \Delta(\Delta H^\circ)_{1\text{Et}_2\text{Tu}} < \Delta(\Delta H^\circ)_{1\text{MeTu}} \sim \Delta(\Delta H^\circ)_{1\text{EnTu}} < \Delta(\Delta H^\circ)_{1\text{Me}_4\text{Tu}} < \Delta(\Delta H^\circ)_{1\text{Tu}} < \Delta(\Delta H^\circ)_{1\text{MeEtTu}}$  and the same for the sequence of stepwise entropy changes. For the reaction series  $\text{AgL}_{(i)} + \text{L}_{(i)} = \text{AgL}_{(i)_2}$  the sequences are almost totally reversed.

The standard enthalpy changes for the stepwise complex formation reactions  $\text{AgL}_{n-1} + \text{L} = \text{AgL}_n$  show less favourable sometimes positive values for the coordination of the second ligand in respect both to the first and the third coordinations. The values are readily counterbalanced by the respective changes in entropy changes which follow the same pattern (Figure 1). From the results by now obtained, the following relationships  $\Delta H_1^\circ < \Delta H_2^\circ > \Delta H_3^\circ$  ( $\Delta S_1^\circ < \Delta S_2^\circ > \Delta S_3^\circ$ ), it can be assumed as general behavior for the stepwise complex formation reactions between  $\text{Ag}(\text{I})$  and substituted thiourea ligands in hard solvents.

Between the enthalpy and the entropy changes, linear compensative relationships occur for the stepwise complex formation (Figure 2).

#### 4. Remarks

The actual results strengthen previous remarks on thermodynamics of complex formation between  $\text{Ag}(\text{I})$  and thioureas in

TABLE 2: Most probable stability constants ( $\log\beta_n$ ,  $\beta_n$  as  $\text{m}^{-n} \cdot \text{dm}^{3n}$ ), standard free energy  $\Delta G^\circ$  (as  $\text{kJ} \cdot \text{m}^{-1}$ ), enthalpy  $\Delta H^\circ$  (as  $\text{kJ} \cdot \text{m}^{-1}$ ), and entropy  $\Delta S^\circ$  changes (as  $\text{kJ} \cdot \text{K}^{-1} \cdot \text{m}^{-1}$ ) at  $T = 298.2 \text{ K}$  and ionic strength self-determined by  $[\text{AgNO}_3] = 6.36 \times 10^{-6} - 3.83 \times 10^{-5} \text{ m} \cdot \text{dm}^{-3}$  for the overall complexing reactions  $\text{Ag}(\text{I}) + n\text{L} = \text{AgL}_n$ .

Ligand	$n$	$\log\beta_n$	$-\Delta G^\circ$	$\Delta H^\circ$	$\Delta S^\circ$
Tu	1	9.9	56.2	$-105 \pm 21$	$-165 \pm 71$
	2	13.7	78.2	$-142 \pm 26$	$-214 \pm 88$
	3	16.1	92	$-140 \pm 17$	$-161 \pm 88$
MeTu	1	9.6	55	$-137 \pm 19$	$-275 \pm 64$
	2	13.4	76.2	$-149 \pm 16$	$-244 \pm 54$
	3	15.9	90.9	$-192 \pm 14$	$-339 \pm 48$
Me <sub>2</sub> Tu	1	8.5	43.8	$-160 \pm 29$	$-373 \pm 97$
	2	12.6	72.3	$-131 \pm 15$	$-197 \pm 50$
	3	15.1	85.9	$-173 \pm 24$	$-292 \pm 80$
Me <sub>4</sub> Tu	1	6.1	36.2	$-122 \pm 29$	$-288 \pm 97$
	2	10.5	60.1	$-103 \pm 17$	$-144 \pm 56$
	3	13.3	76.1	$-165 \pm 53$	$-298 \pm 177$
EtTu	1	9.5	54.5	$-72 \pm 27$	$-59 \pm 90$
	2	13.6	77.5	$-121 \pm 12$	$-146 \pm 42$
	3	16.3	93.1	$-153 \pm 20$	$-201 \pm 60$
Et <sub>2</sub> Tu	1	9.6	55.0	$-157 \pm 24$	$-342 \pm 80$
	2	13.6	77.4	$-134 \pm 42$	$-188 \pm 140$
	3	16.3	95.1	$-186 \pm 25$	$-305 \pm 81$
EnTu	1	11.5	65.9	$-134 \pm 24$	$-230 \pm 80$
	2	15.3	87.3	$-144 \pm 12$	$-190 \pm 41$
	3	17.2	98.3	$-233 \pm 38$	$-452 \pm 130$

hydroxyl hard solvents and the tendency of the complexed central ion to bind further ligand [10–15]. The substratum to ligand affinities is contained within ranges of free energy changes which are related to the coordination levels of the substrata: the higher the coordination level of the reacting substrata, the narrower the amplitude of the free energy ranges. In addition, more thermodynamically stable is the coordinatively unsaturated reacting substratum, lower is the tendency to coordinate further ligands. So, it can be affirmed that the coordinated ligands affect the coordinating ability of the central ion in inverse way to their global mutual affinity towards the central ion. In some cases the influence leads to nonlinear (exponential) free energy relationships [14, 15] and coordinatively unsaturated, but very stable complexes for very high metal-to-ligand affinities do not bind further ligands although the central ion is not exhaustively coordinated.

The comparatively examined substratum-to-ligand affinity sequences (Figure 1) at coordination level of the reacting substratum  $n = 0$  or  $n = 1$  confirm the stated sentence: to higher (lower) affinity of the ligand L towards Ag(I) with respect to ligand L' at  $n = 0$  ( $\Delta G^\circ$  for the reaction  $\text{Ag}(\text{I}) + \text{L} = \text{AgL} >(<) \Delta G^\circ$  for the reaction  $\text{Ag}(\text{I}) + \text{L}' = \text{AgL}'$ ) it corresponds reversed affinity sequence of the same ligands towards the respective mono-coordinated substrata. On comparing the sequences for mono- and biscoordinated substrata, identical behaviors are found.

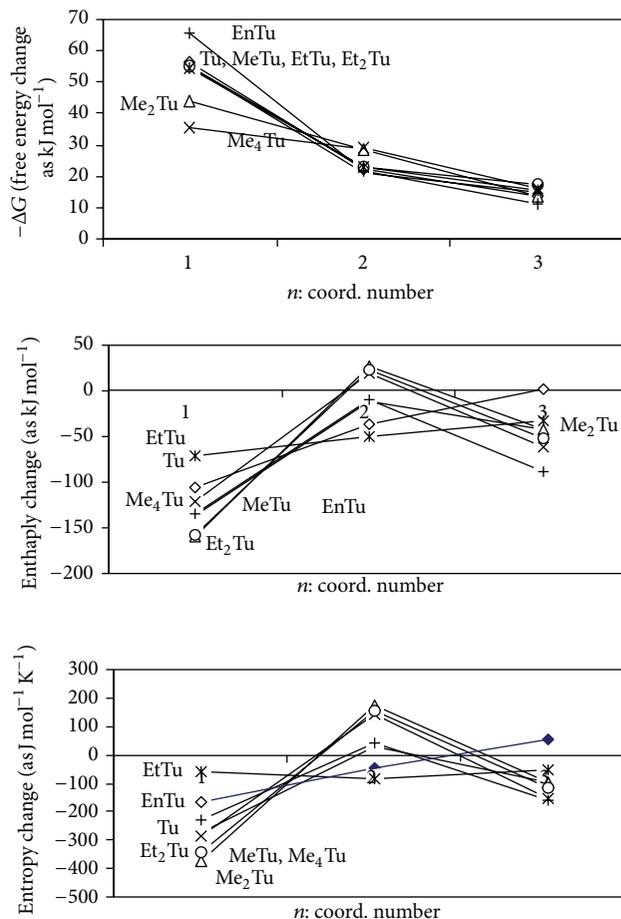


FIGURE 1: Free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ) changes for the stepwise complex formation reactions  $\text{AgL}_{n-1} + \text{L} = \text{AgL}_n$  at  $t = 25^\circ \text{C}$  and various coordination levels (data from Table 2). The general sequence of the substratum to ligand affinity, enthalpy, and entropy changes (i) in the reactions of  $\text{AgL}_n$  ( $n = 1-3$ ) substrata with the same ligands as dependent on the coordination level of the reacting substratum, (ii) in the reactions  $\text{AgL}_{(i)n-1} + \text{L} = \text{AgL}_{(i)n}$  ( $n = 1-3$ ) in dependence on the alkyl substitution at the same coordination level and (iii) the concurrent changes in the corresponding  $\Delta H^\circ$  and  $\Delta S^\circ$  are evident. Such parallelism in the  $\Delta H^\circ$  and  $\Delta S^\circ$  occurs very often in homologous series of reactions [10–13].

The enthalpy changes show exothermic overall complex formation reactions but at the same time temperature unfavoured (negative entropy changes). The dissection in successive stepwise contribution for single ligand complexing reactions  $\text{AgL}_{n-1} + \text{L} = \text{AgL}_n$  discloses unmonotonous trend in dependence on the coordination level  $n$ : the first and third coordination (Figure 1) are more enthalpy favoured (entropy disfavoured), whereas the second coordination involves less favorable sometimes positive enthalpy changes counterbalanced by more favorable sometimes positive entropy changes.

By taking into account the compensative enthalpy-entropy relationships (Figure 2), it can be concluded that the systems maintain their stiffness on the occurrence of the first and third coordination whilst the stiffness is lost on the second complexing reaction. Probably the solvation of

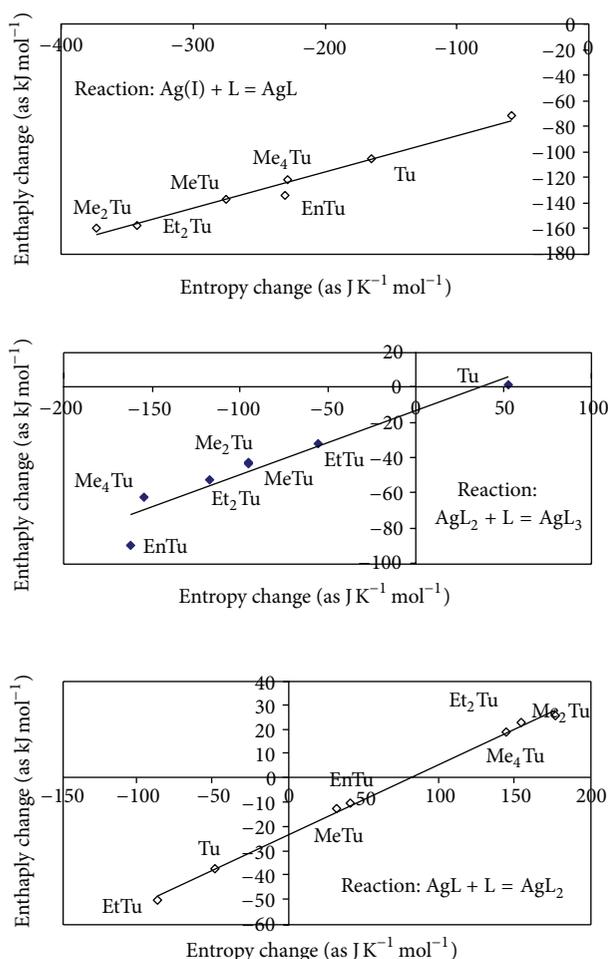


FIGURE 2:  $\Delta H^\circ - \Delta S^\circ$  isoequilibrium relationships in the series of stepwise complex formation reactions  $\text{AgL}_{n-1} + \text{L} = \text{AgL}_n$  at the coordination level  $n = 1-3$ . In parenthesis, standard deviations are reported. For the series  $\text{Ag(I)} + \text{L}_{(i)} = \text{AgL}_{(i)}$  ( $\text{L}_{(i)}$  = variable):  $\Delta H^\circ = -58.5(\pm 9.4) + 0.285(\pm 0.04)\Delta S^\circ$  ( $R^2 = 0.988$ ;  $T_{\text{iso}} = 285 \text{ K}$ ); for the series  $\text{AgL}_{(i)} + \text{L} = \text{AgL}_{(i)2}$  ( $\text{L}_{(i)}$  = variable):  $\Delta H^\circ = -22.9(\pm 2.6) + 0.305(\pm 0.01)\Delta S^\circ$  ( $R^2 = 0.999$ ;  $T_{\text{iso}} = 305 \text{ K}$ ); for the series  $\text{AgL}_{(i)2} + \text{L}_{(i)} = \text{AgL}_{(i)3}$  ( $\text{L}_{(i)}$  = variable):  $\Delta H^\circ = -12.8(\pm 5.7) + 0.365(\pm 0.05)\Delta S^\circ$  ( $R^2 = 0.953$ ;  $T_{\text{iso}} = 365 \text{ K}$ ). (R: Corr. Coeff.;  $T_{\text{iso}}$ : isoequilibrium temperature).

the respective reacting substratum is maintained during the first and third coordination and sensitive desolvation process occurs in the second coordination.

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