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Short communication

Complex formation equilibria between Ag(I) and thioureas in *n*-propanol

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Abstract

Complex formation equilibria between Ag(I) and thiourea or *N*-alkyl-substituted thioureas have been investigated in *n*-propanol by potentiometry at 10 °C intervals from 5 to 50 °C. Stepwise formation of tris-coordinated AgL_n ($n = 1–3$) complexes has been found for the majority of the ligands. ΔH and ΔS values for the complex formation reactions have been evaluated from the dependence of $\ln \beta_n$ on temperature. The alkyl-substituents affect the ligand affinities in different ways in relation with the coordination level n.

The reactions are exothermic with few exceptions. Enthalpy favoured complex formation with negative dependence of ΔG on temperature ($\Delta S > 0$) have been found.

The enthalpy and entropy changes for the stepwise complex formation equilibria are correlated by two linear compensative relationships with the same isoequilibrium temperature 50–51 °C.

Keywords: Ag complexes; *n*-Propanol; Enthalpy–entropy relationship

1. Introduction

Systematic investigations of selected equilibria in related solvents can contribute to the rationalisation of the solvent effect [1–6]. Complex formation equilibria of Ag(I) and *N*-alkyl-substituted thiocarbonyl ligands in the protic solvents H_2O, methanol and ethanol have been previously investigated [7–10]. In this contribution the results of investigations on the thermodynamics of complex formation equilibria between Ag(I) and thiourea or *N*-alkyl-substituted thioureas in *n*-propanol are reported.

2. Experimental

2.1. Chemicals

$AgNO_3$ and ligands were commercial products with purity grade >99.8%. Ag(I) and ligand solutions were prepared by direct weighing. *n*-Propanol has water content <0.1%.

2.2. Measurements and calculations

Potentiometric measurements were performed in a thermostated cell with the electrode system:

$$\begin{aligned} \mathrm{Ag}|[\mathrm{AgNO_3}]_{\mathrm{tot}} &= \text{const.}, [\mathrm{L}]_{\mathrm{tot}} \\ &= \text{var. in } n\text{-propanol (test cell)}|\mathrm{LiNO_3}\text{ sat.,} \\ &\quad \text{saltbridgein } n\text{-propanol}|\mathrm{KCl}\text{ sat.,} \\ &\quad \text{aqueoussolution (ref. cell)}|\mathrm{Ag} \end{aligned}$$

Five different solutions with equally spaced $[Ag(I)]_{tot}$ within the range 5×10^{-6} to 3×10^{-5} M were titrated at each temper-

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Abbreviations: Tu, thiourea; MeTu, *N*-methylthiourea; Me_2Tu, *N*,*N*′-dimethylthiourea; Me_4Tu, *N*,*N*,*N*′,*N*′-tetramethylthiourea; EtTu, *N*-ethylthiourea; Et_2Tu, *N*,*N*′-diethylthiourea; EnTu, ethylenethiourea; $IsPr_2Tu$, *N*,*N*′-diisopropylthiourea; ALTu, *N*-allylthiourea; Bu_2Tu, *N*,*N*′-dibutylthiourea; TBu_2Tu, *N*,*N*′-diterbutylthiourea

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ature with 10^{-2} M ligand solution (ligand concentration range: $1.33 \times 10^{-4}\,\mathrm{M} \leq [\mathrm{L}]_{\mathrm{tot}} \leq 1.8 \times 10^{-3}\,\mathrm{M}$). No background electrolyte was added to the solutions. The data in the tables refer to the ionic strength range $\mu = 5 \times 10^{-6}$ to 3×10^{-5}.

The set of $\{\Delta E_{\mathrm{exp}}, [\mathrm{L}]_{\mathrm{tot}}, [\mathrm{Ag(I)}]_{\mathrm{tot}}\}$ data at each temperature were processed by a nonlinear least square computer program that minimizes the sum of the experimental residuals $\sum_i(\Delta E_{\mathrm{exp}} - \Delta E_{\mathrm{cal}})_i^2$ where

$$\Delta E_{\mathrm{cal}} = \Delta E_0 + \frac{RT}{nF} \ln \frac{[\mathrm{Ag(I)}]_{\mathrm{tot}}}{\sum_n \mathrm{e}^{\ln \beta_n} [\mathrm{L}]_{\mathrm{free}}}$$

to obtain the best values of ΔE_0 and $\{\ln \beta_n\}$. The values of the parameters were refined until constant within five digits and the calculated ΔE_0 value was consistent with the deduced value from experimental relationships ΔE_{exp} versus $\ln[\mathrm{Ag(I)}]_{\mathrm{tot}}$ in absence of ligand. The perfect agreement of the experimental deduced angular coefficient of the ΔE_{exp} versus $\ln[\mathrm{Ag(I)}]_{\mathrm{tot}}$ relationship with the theoretical value from Nernst equation proves the reversibility of the electrode system Ag/Ag(I) in *n*-propanol. Further detail about methods and calculations can be found in Refs. [7–9] or obtained directly from the authors.

3. Results and discussion

The experimental $\{\Delta E_{\mathrm{exp}}, [\mathrm{L}]_{\mathrm{tot}}, [\mathrm{Ag(I)}]_{\mathrm{tot}}\}$ data can be interpreted with three AgL_n ($n = 1$–3) complexes at each temperature with the exclusion of the systems Ag(I)–IsPr$_2$Tu and Ag(I)–TBu$_2$Tu where it is sufficient to hypothesize the presence of only two complexes AgL_n ($n = 1$–2). Table 1 gives the $\ln \beta_n$

Table 1
Stability constants $\ln \beta_n$ (β_n as $\mathrm{dm}^{3n}\,\mathrm{mol}^{-n}$) for the overall complex formation reactions $\mathrm{Ag(I)} + n\mathrm{L} = \mathrm{AgL}_n$ between Ag(I) and thioureas at different temperatures and ionic strength $\mu = 5 \times 10^{-6}$ to 3×10^{-5} in *n*-propanol, and ΔG (at 25 °C as $\mathrm{kJ\,mol^{-1}}$), ΔH (as $\mathrm{kJ\,mol^{-1}}$) and ΔS (as $\mathrm{J\,mol^{-1}}$) calculated from the linear dependence of $\ln \beta_n$ on T^{-1} ($\ln \beta_n = \Delta S/R - (\Delta H/R)T^{-1}$)

Ligand	n	5 °C	15 °C	25 °C	35 °C	45 °C	50 °C	$\ln \beta_{n(\mathrm{cal})}$	$-\Delta G$ (25 °C)	ΔH	ΔS
1. Tu	1	29.6 ± 1.3	27.0 ± 0.7	25.9 ± 1.5	25.0 ± 1.0	24.1 ± 1.2	–	26.1	63.6	92	−91
	2	37.9 ± 1.0	35.5 ± 0.8	33.9 ± 1.3	30.1 ± 1.5	30.3 ± 1.0	–	33.3	81.1	−142	−199
	3	43.1 ± 0.2	40.6 ± 1.0	38.5 ± 1.2	38.0 ± 0.8	35.9 ± 1.0		38.9	94.9	−117	−69
2. MeTu	1	28.3 ± 0.3	27.7 ± 0.7	26.5 ± 1.0	24.7 ± 0.7	24.7 ± 1.0	–	26.2	64	−71	−18
	2	37.3 ± 0.6	35.8 ± 0.5	33.3 ± 0.8	32.0 ± 0.6	30.3 ± 1.2	–	33.5	81.6	−122	−131
	3	43.5 ± 0.5	40.8 ± 0.7	39.2 ± 0.6	36.6 ± 0.7	36.2 ± 0.8	–	39	95	−130	−112
3. Me$_2$Tu	1	23.5 ± 1.7	25.2 ± 1.2	24.4 ± 0.7	23.3 ± 0.7	–	22.2 ± 0.7	24.3	59.1	−69	−29
	2	34.4 ± 1	33.4 ± 1.0	32.2 ± 0.5	30.8 ± 1.1	–	28.1 ± 0.7	31.7	77.2	−96	−58
	3	40.2 ± 0.5	39.2 ± 0.8	36.3 ± 1.4	36.1 ± 1.0	–	33.6 ± 0.3	37	90.1	−104	−41
4. Me$_4$Tu	1	20.0 ± 1.1	19.3 ± 1.1	18.1 ± 2.1	17.6 ± 1.1	16.3 ± 1.1	15.7 ± 0.7	18.0	43.9	−67	−75
	2	28.6 ± 0.6	27.0 ± 0.9	25.0 ± 1.2	24.0 ± 1.3	23.8 ± 0.7	23.3 ± 0.6	25.6	62.3	−82	−62
	3	35.6 ± 0.5	34.2 ± 0.8	32.7 ± 0.6	30.9 ± 0.9	29.6 ± 0.9	28.7 ± 0.5	32.3	78.6	−107	−92
5. EtTu	1	26.0 ± 1.2	24.2 ± 1.0	23.5 ± 0.8	22.6 ± 0.7	21.7 ± 1.0	19.1 ± 1.8	23.1	56.4	−90	−110
	2	34.8 ± 0.8	34.2 ± 0.6	32.6 ± 0.5	31.0 ± 0.5	29.9 ± 0.7	29.2 ± 0.9	32.3	78.9	−91	−38
	3	42.1 ± 0.7	40.5 ± 0.7	38.4 ± 1.1	36.8 ± 0.6	35.9 ± 0.6	–	38.5	93.7	−110	−49
6. Et$_2$Tu	1	20.6 ± 1.7	20.8 ± 1.3	17.8 ± 1.5	18.8 ± 0.9	17.7 ± 1.1	20.1 ± 1.5	19.4	47.2	−28	+67
	2	34.2 ± 0.7	31.8 ± 0.5	30.6 ± 0.6	29.1 ± 0.4	28.0 ± 0.7	27.4 ± 1.3	30.5	74.4	−103	−93
	3	40.2 ± 0.6	38.8 ± 0.6	36.4 ± 0.8	34.3 ± 0.6	33.0 ± 0.9	35.5 ± 1.1	30.7	89.4	−100	−30
7. EnTu	1	21.8 ± 1.4	21.1 ± 1.5	19.2 ± 1.7	20.4 ± 0.8	20.91 ± 0.6	18.1 ± 1.4	20.3	49.6	−37	+14
	2	34.2 ± 0.7	33.1 ± 0.6	31.5 ± 0.6	30.3 ± 0.5	29.2 ± 0.8	28.4 ± 0.6	31.5	76.6	−89	−38
	3	40.2 ± 0.6	38.7 ± 1.0	36.4 ± 0.4	34.1 ± 0.3	–	–	36.1	88.	−129	−134
8. ALTu	1	24.7 ± 0.6	22.6 ± 1.1	21.3 ± 1.0	22.1 ± 0.7	21.1 ± 1.0	21.3 ± 0.9	22.3	54.0	−49	+23
	2	33.4 ± 1.3	32.5 ± 0.4	31.7 ± 0.5	29.8 ± 0.4	28.7 ± 0.6	27.8 ± 0.8	32.6	79.5	−90	−27
	3	40.4 ± 0.4	38.4 ± 0.6	36.5 ± 1.0	35.5 ± 0.7	33.7 ± 0.9	33.4 ± 0.7	36.7	89.4	−110	−64
9. IsPr$_2$Tu	1	23.0 ± 0.9	20.4 ± 1.1	19.0 ± 1.6	19.6 ± 1.1	18.9 ± 1.3	18.7 ± 1.2	20.1	49.0	−59	−32
	2	32.1 ± 0.6	29.4 ± 0.7	28.8 ± 0.7	26.8 ± 0.8	26.8 ± 0.8	25.2 ± 0.9	20.1	49.0	−59	−32
	3	–	–	–	34.4 ± 0.4	32.8 ±	–	28.6	69.7	−97	−76
10. BuTu	1	25.8 ±	24.6 ± 0.9	24.4 ± 0.9	22.6 ± 1.4	22.1 ± 0.8	21.4 ± 0.5	23.7	57.7	−67	−29
	2	34.1 ± 1.2	33.3 ± 1.3	31.3 ± 0.9	31.6 ± 1.0	29.2 ± 0.9	29.0 ± 0.6	31.7	77.2	−81	−7
	3	41.1 ± 0.8	39.1 ± 0.9	38.7 ± 1.0	37.6 ± 1.1	35.8 ± 0.6	34.7 ± 0.6	38.1	99.8	−92	+7
11. Bu$_2$Tu	1	23.7 ± 0.8	22.5 ± 0.9	21.7 ± 2.0	20.6 ± 0.7	19.1 ± 1.0	18.9 ± 1.0	21.4	52.0	−77	−81
	2	33.0 ± 0.6	31.9 ± 0.5	30.5 ± 1.0	29.1 ± 0.6	33.0 ± 0.6	31.9 ± 0.5	30.1	73.3	−97	−74
	3	39.4 ± 0.6	37.5 ± 0.8	36.1 ± 0.5	34.2 ± 1.2	33.6 ± 1	32.7 ± 0.6	36	87.6	−103	−47
12. TBu$_2$Tu	1	–	25.8 ± 0.3	25.6 ± 0.4	22.0 ± 1.1	22.3 ± 1.4	24.9 ± 1.4	24.5	59.1	−48	+42
	2	32.7 ± 1.8	35.5 ± 0.7	34.3 ± 0.7	33.5 ± 0.5	32.5 ± 0.7	32.3 ± 1.0	34.2	83.3	−69	+49
	3	41.4 ± 1.3	–	–	–	–	–				

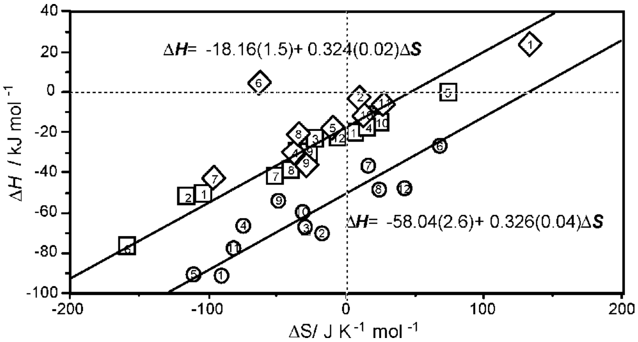

Fig. 1. ΔH vs. ΔS for the stepwise complex formation equilibria between Ag(I) and thioureas in *n*-propanol ($T_{\mathrm{iso}} = 50–51\,°\mathrm{C}$). Standard deviations are reported in parentheses. For the numbers refer to the list of symbols. Circle: $n = 1$; square: $n = 2$; rohmb: $n = 3$. Numbers refer to Table 1.

values for the formation of the complexes and the dependence of $\ln \beta_n$ on T^{-1} together with ΔG (at 25 °C), ΔH and ΔS.

ΔH_n, ΔS_n for the stepwise complex formation reactions are linearly interdependent and form two parallel compensative relationships with the same isoequilibrium temperature [11,12] 50–51 °C (Fig. 1). The lower line includes the first coordination reaction series $\mathrm{Ag(I)} + \mathrm{L}(i) = \mathrm{AgL}(i)$. The higher line includes the second and third series of stepwise coordination reactions.

The ligand affinity sequences depend on the coordination number n and reflect the ones found for the same systems in other protic solvents [7–9]. The affinity sequences of the ligands towards Ag(I) ($n = 0$) compared with the corresponding affinity sequences towards the monocoordinated AgL(i) substrata ($n = 1$) are in general mutually reversed. A greater affinity of L(i) towards Ag(I) corresponds to lower affinity of the same ligand towards AgL(i).

Thiocarbonyl ligands coordinate to Ag(I) via the sulphur atom [13], but the alkyl-substituents on the nitrogen atoms influence the ligand affinities. In the first coordination reactions $\mathrm{Ag(I)} + \mathrm{L(i)} = \mathrm{AgL(i)}$, the influence of the alkyl groups is contained within the range of $\sim$20 kJ mol^{-1} between the lowest value (~ -64 kJ mol^{-1}) for the complex formation reaction $\mathrm{Ag(I)} + \mathrm{Tu} = \mathrm{AgTu}$ or $\mathrm{Ag(I)} + \mathrm{MeTu} = \mathrm{AgMeTu}$ and the highest value (~ -44 kJ mol^{-1}) for the reaction $\mathrm{Ag(I)} + \mathrm{Me_4Tu} = \mathrm{AgMe_4Tu}$. In the stepwise formation of bis-coordinates $\mathrm{AgL(i)} + \mathrm{L(i)} = \mathrm{AgL(i)_2}$ the range reduces to $\sim$10 kJ mol^{-1} between ~ -17 kJ mol^{-1} for the reactions $\mathrm{AgTu} + \mathrm{Tu} = \mathrm{AgTu_2}$ or $\mathrm{AgMeTu} + \mathrm{MeTu} = \mathrm{Ag(MeTu)_2}$ and ~ -25 kJ mol^{-1} for the reaction $\mathrm{AgEtTu} + \mathrm{EtTu} = \mathrm{Ag(EtTu)_2}$ or $\mathrm{AgEnTu} + \mathrm{EnTu} = \mathrm{Ag(EnTu)_2}$. For stepwise formation of tris-coordinates $\mathrm{AgL(i)_2} + \mathrm{L(i)} = \mathrm{AgL(i)_3}$ the free energy changes are scattered within 10 kJ mol^{-1}, but the sequence of ligands does not seem to be related to the previous series. The reactions with Tu or MeTu show similar free energy changes with central position in the affinity sequence.

The enthalpy–entropy relationships of Fig. 1 show that the first, second and third stepwise complex formation reaction series have the same isoequilibrium temperature.

The occurrence of an isoequilibrium temperature has the following consequences: (i) the affinity sequences are specularly reversed between $T < T_{\mathrm{iso}}$ and $T > T_{\mathrm{iso}}$ and (ii) the divergence in the free energy changes between the various reactions is proportionally related to $T - T_{\mathrm{iso}}(\Delta(\Delta G) = \alpha(T - T_{\mathrm{iso}}))$.

The majority of the overall and stepwise complex formation reactions of Ag(I) with thioureas are exothermic in nature so that the reactions results disfavoured by increasing the temperature but some of them are both enthalpy and entropy favoured.

The changes in ΔH and ΔS between the first and second stepwise coordination $\mathrm{AgL(i)}_{n-1} + \mathrm{L(i)} = \mathrm{AgL(i)}_n$ ($n = 1, 2$) and the changes in the corresponding second and third stepwise coordination ($n = 2, 3$) are mutually reversed; $\Delta H_2 < \Delta H_1$ corresponds $\Delta H_3 > \Delta H_2$. A similar statement supplies to the entropy changes.

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