Thermodynamics of Complex Formation of Silver with Amines in Dimethyl Sulphoxide

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Equilibrium constants, enthalpy changes, and entropy changes have been determined for the complex formation between silver and a number of amines in dimethyl sulphoxide (dmso) at 25 °C. The ionic strength of the solutions was kept at 0.1 mol dm^{-3} with tetraethylammonium perchlorate. All the complexes are enthalpy stabilized, whereas the entropy contributions oppose the complex formation. The values of the thermodynamic parameters obtained in dmso are compared with those for the same systems in aqueous solution. The data are also discussed in relation to the different solvations of the species in water and dmso.

The thermodynamics of complex formation between silver and nitrogen-donor ligands such as amines has been extensively investigated in water.[1–4] The stabilities of the complexes formed in aqueous solution are in general due to favourable enthalpy terms, whereas the entropy contributions oppose the complex formation, usually quite strongly.

The formation of metal complexes depends very much upon the solvation of the species involved in the reactions which in turn depends upon the nature of the solvent and the species concerned.[5,6] A strong solvation, for instance, is to be expected in protic solvents such as water, for species apt to form hydrogen bonds.[6] As the complex formation between metal ions and ligands occurs in competition with the solvation of the species involved, the thermodynamics of metal complex formation in solution is of course influenced by the solvation. For instance, the trend observed in aqueous solution for a given acceptor with a series of ligands can be completely reversed in aprotic solvents.[7,8] The influence of solvation can be studied by performing the same reactions in solvents with different donor properties.

In the present investigation the thermodynamics of complex formation between silver and a number of monoamines in the aprotic solvent dimethyl sulphoxide (dmso) has been studied. The ligands investigated are n-butylamine, dibutylamine, piperidine, morpholine, and pyridine. The aim was first to determine the thermodynamic functions for silver complex formation with nitrogen-donor ligands in dmso as such data are not available in the literature, then to get a better understanding of the solvent effect on the metal complex formation, and finally to compare the data obtained with the corresponding values previously found for the same systems in aqueous solution. The stability constants for the systems investigated, and therefore the free-energy changes, have been determined by potentiometry, the enthalpy changes accompanying the complex formation by direct calorimetric titrations. The investigation was performed at 25 °C and in a medium of ionic strength 0.1 mol dm^{-3} with tetraethylammonium perchlorate.

Experimental

Chemicals.—Commercially available $AgClO_4 \cdot H_2O$ was dried *in vacuo* at 50 °C for several days and used without further purification. The ligands were purified according to methods reported previously.[9] The ligand solutions were standardized by thermometric titrations with standard $HClO_4$ solution.

The dmso was distilled over calcium hydride under reduced pressure and kept over 3A molecular sieves. Tetraethylammonium perchlorate was recrystallized from CH_3OH and dried at 110 °C. The silver content in the $AgClO_4$ stock solution was periodically checked by potentiometric titrations with a standard solution of NaCl.

Solutions of the ligands were prepared by dissolving known amounts of them in freshly distilled dmso and the ionic strength was adjusted to 0.1 mol dm^{-3} by adding the appropriate amount of NEt_4ClO_4.

Potentiometric Measurements.—The experimental data for the determination of the stability constants of the systems investigated were obtained by mean of the cell shown in the Scheme. The salt bridge was of the Whilhelm type.[10] A PHM 84 Radiometer was used for the e.m.f. measurements.

(−)Ag	c_M mmol dm^{-3} $AgClO_4$	NEt_4ClO_4	$AgClO_4$	Ag(+)
	c_L mmol dm^{-3} L	0.1 mol dm^{-3}	0.1 mol dm^{-3}	
	I = 0.1 mol dm^{-3}			

Scheme. L = amine

The e.m.f. of the cell can be expressed as $E = E_r - 59.16 \log [Ag^+]$, where E_r is the potential of the reference electrode. The liquid-junction potential was found to be negligible. Stable readings were usually obtained within 5 min in the most favourable cases, 20 min in the least favourable ones. E.m.f. measurements were also carried out in order to check that in dmso the silver electrode behaved according to Nernst's law. No significant deviations were found in the range $10^{-5} \leqslant [Ag^+] \leqslant 10^{-2}$ mol dm^{-3}.

Ingold vessels with outer jackets were used for the electrolyte solutions. The titrations were performed by adding known volumes of ligand solutions of concentration c_L° to silver solutions of known concentration c_M° in the right hand side half-cell. For each ligand at least three different values of c_M° and c_L° were employed. The reproducibility was better than 0.20 mV for low values of $c_L : c_M$ and better than 0.3 mV for higher ones.

The least-squares program Miniquad[11] was used for calculation of the stability constants.

Calorimetric Measurements.—The calorimetric measurements were made using a Tronac precision titration calorimeter, model 87-558, equipped with a 25-cm^3 titration vessel. All the experiments were carried out at 25.000 ± 0.001 °C. The calorimetric titrations were performed by adding, to a silver perchlorate solution of concentration c_M°, ligand solutions of concentration c_L° at a constant rate of 0.2116 cm^3 min^{-1}. For each system investigated at least five titration series were performed with c_M° varying from 5 to 20 mmol dm^{-3} and c_L° from 10 to 150 mmol dm^{-3}.

The experimental values of the heat changes were corrected for the heats of dilution of the ligand solutions, determined separately. The heat of dilution of silver perchlorate solutions was negligible in the metal concentration range used here.

The enthalpy changes for the systems investigated were calculated using the least squares program LETAGROP Kalle.[12]

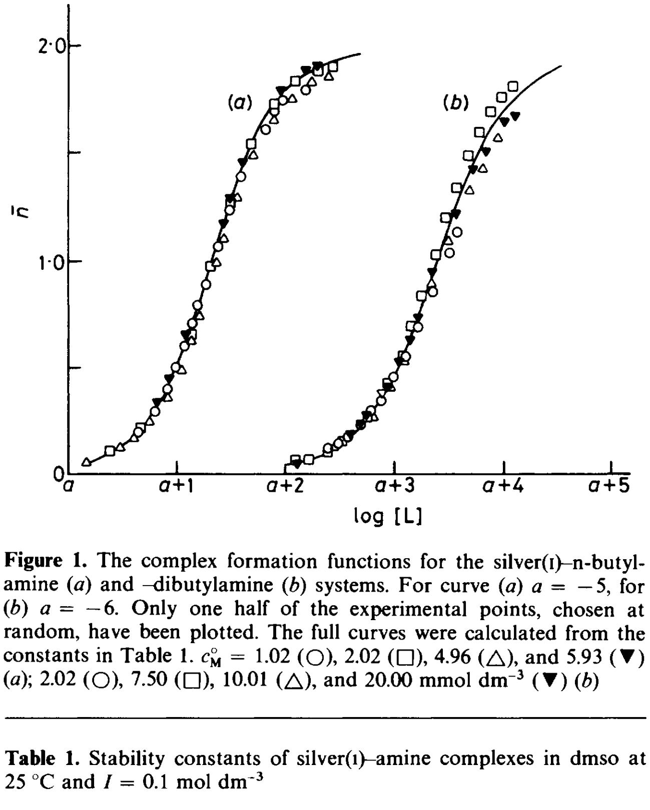

Figure 1. The complex formation functions for the silver(I)–n-butylamine (*a*) and -dibutylamine (*b*) systems. For curve (*a*) $a = -5$, for (*b*) $a = -6$. Only one half of the experimental points, chosen at random, have been plotted. The full curves were calculated from the constants in Table 1. c_M° = 1.02 (○), 2.02 (□), 4.96 (△), and 5.93 (▼) (*a*); 2.02 (○), 7.50 (□), 10.01 (△), and 20.00 mmol dm^{-3} (▼) (*b*)

Table 1. Stability constants of silver(I)–amine complexes in dmso at 25 °C and I = 0.1 mol dm^{-3}

Ligand	log K_1	log K_2
n-Butylamine	3.58	3.76
Dibutylamine	2.66	2.50
Piperidine	3.11	2.94
Morpholine	2.58	2.10
Pyridine	1.41	0.70

Results and Discussion

The complex formation curves for the systems investigated are shown in Figures 1 and 2. The average number of ligands, $\bar{n}$, the free-ligand concentration, as well as a preliminary evaluation of the stability constants of the silver(I) complexes have been obtained according to a graphical method reported previously.[13,14] The stability constants were then refined by means of a computer program.[11]

The final values of the stepwise equilibrium constants, log K_n, are given in Table 1. The free-energy, enthalpy, and entropy changes are listed in Table 2; for comparison, the results of earlier investigations in aqueous solution are also included. Within the silver and ligand concentration ranges investigated, only two mononuclear complexes are formed and $K_1/K_2 \approx 1$ for all the systems.

A common feature of all the systems is that the formation of the silver complexes with amines, both in dmso and water, is strongly exothermic, whereas the entropy terms, with the exception of the first step for silver–n-butylamine in water, are negative and therefore oppose the complex formation. This trend is the one expected for the complex formation of typically soft acceptors such as silver(I), in protic and aprotic solvents, as a result of both the formation of strong co-ordinate bonds of marked covalent character and the weak solvation of the species involved in the complex formation. The weak solvation, especially of the ligands, is also reflected in the unfavourable entropy contributions.

The lower stability of the first silver complex with the secondary amine dibutylamine compared to that formed with the primary amine, n-butylamine, is mainly due to a more unfavourable entropy term as the enthalpy changes, in spite of the weaker basicity of the secondary amine in dmso,[15–17] are of the same order of magnitude for both systems. Earlier investigations[15] indicate the formation of hydrogen bonds between dmso and the amine-group hydrogens. These bonds are much stronger for the primary than for the secondary amines. The higher solvation of the primary amine in addition to increasing steric restrictions as the ligand becomes more and more bulky explains the results obtained in this work.

The strength of the complexes formed by silver(I) with piperidine (pip), morpholine (morph), and pyridine (py), decreases in the order pip > morph > py, reflecting the decreasing strength of the Ag–L bond and indicating that piperidine is a better donor.

A characteristic feature of all the systems in dmso, except for the silver–dibutylamine complexes, is that $-\Delta H_2^\circ \gg -\Delta H_1^\circ$. This is probably due to a specially large desolvation occurring in the first step of complexation, indicating that the enthalpy needed for the desolvation is so large that ΔH_1° becomes less exothermic in spite of the fact that the heat evolved in the silver–amine bond formation is certainly large in the first step. That

Table 2. Thermodynamic functions for the stepwise formation of silver(I)–amine complexes in dmso and water (ref. 3) at 25 °C and I = 0.1 mol dm^{-3}; ΔG_n° and ΔH_n° in kJ mol^{-1}, ΔS_n° in J K^{-1} mol^{-1}

		dmso			Water		
Ligand	n	$-\Delta G_n^\circ$	$-\Delta H_n^\circ$	$-\Delta S_n^\circ$	$-\Delta G_n^\circ$	$-\Delta H_n^\circ$	$-\Delta S_n^\circ$
n-Butylamine	1	20.46	31.40	37.2	19.60	16.70	−8.4
	2	21.42	40.10	62.4	25.90	36.00	25.1
Dibutylamine	1	15.17	31.80	56.0			
	2	14.26	29.80	51.5			
Piperidine	1	17.72	26.30	28.0	17.67	22.18	16.7
	2	16.76	34.10	58.6	19.50	28.02	25.1
Morpholine	1	14.70	24.85	33.9	23.83		
	2	11.95	30.71	62.8	15.57		
Pyridine	1	8.03	13.93	19.7	11.74	20.00	27.6
	2	4.02	27.00	77.0	12.09	27.11	50.6

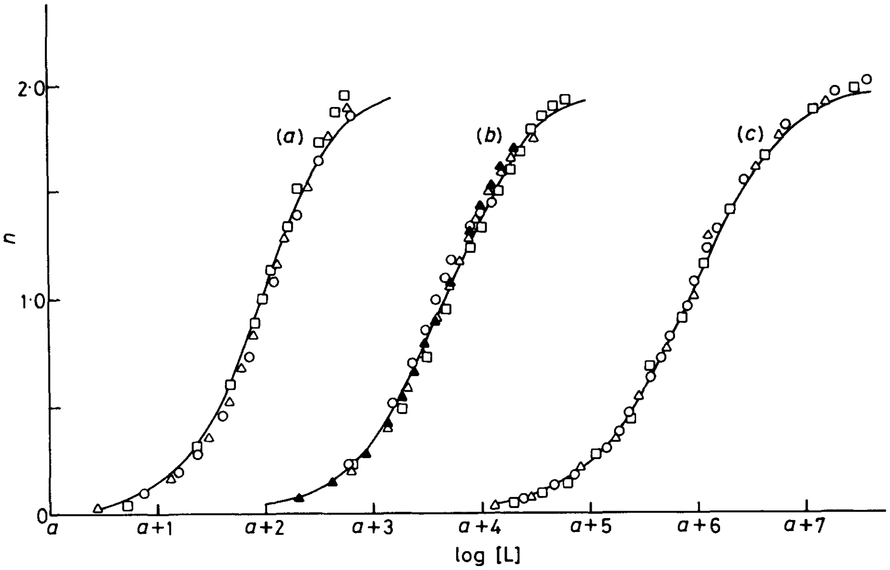

Figure 2. The complex formation functions for the silver(I)–piperidine (*a*), –morpholine (*b*), and –pyridine (*c*) systems. For curve (*a*) $a = -5$, for (*b*) $a = -6$, and for (*c*) $a = -7$. c°_{M} = 2.42 (○), 4.73 (□), and 9.03 (△) (*a*); 2.48 (○), 4.96 (□), 9.93 (△), and 19.85 (▲) (*b*); 4.96 (○), 9.93 (□), and 19.85 mmol dm^{-3} (△) (*c*)

this is the reason for the trend found for the $-\Delta H_2^{\circ}$ values is confirmed by the huge change occurring in the values of the entropy terms between the first and the second step ($-\Delta S_2^{\circ} \gg -\Delta S_1^{\circ}$).

The very similar stabilities of the silver–amine complexes found in water and in dmso (Table 2) is somewhat surprising. Owing to the stronger donating properties of dmso as compared to water, reflected in the very exothermic heat of transfer of Ag^+ from water to dmso,[18] $\Delta H_{tr}^{\circ} = -54$ kJ mol^{-1}, a lower stability of the silver complexes with amines in dmso is expected. This is not the case: the unexpected similarity of the stability constants is presumably connected with a larger solvation of the amines in water, through strong hydrogen bonds, which compensates for the strong solvation of Ag^+ in dmso: this seems to be confirmed by a more unfavourable entropy change in dmso.

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