Equilibrium Measurements for Silver(I) Complexes with Polyamines in Dimethyl Sulphoxide

Alberto Cassol, Plinio Di Bernardo, and Pierluigi Zanonato
Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, via Marzolo 1, I-35131 Padova, Italy
Roberto Portanova* and Marilena Tolazzi
Istituto di Chimica, Università di Udine, Viale Ungheria 43, I-33100 Udine, Italy
Giuliana Tomat
Istituto di Chimica e Tecnologia dei Radioelementi del CNR, C.so Stati Uniti, I-35100 Padova, Italy

The stability constants of silver(I) complexes with 1,2-diaminoethane (en), 1,3-diaminopropane (tn), and diethylenetriamine (dien) in dimethyl sulphoxide (dmso) at 25 °C and at an ionic strength of 0.1 mol dm^{-3} have been determined by potentiometry. Within the silver and ligand concentration ranges investigated, two mononuclear complexes have been found for the Ag^+–en and –dien systems; with tn, polynuclear complexes are formed in addition to a mononuclear species. The ligands all behave as chelating agents, en forming a five-membered chelate ring and tn a six-membered one; dien co-ordinates as a terdentate ligand. All the complexes are stronger in dmso than in water. The effects of the two solvents on the interaction between silver(I) and N-donor ligands are discussed.

In a previous paper[1] the changes in free energy, enthalpy, and entropy for the complex formation between silver(I) and some primary and secondary amines in the aprotic solvent dimethyl sulphoxide (dmso) were reported and the results compared with those obtained earlier for the same systems in aqueous solution. It was shown that in dmso the silver(I) complexes with primary amines are much stronger than those with secondary ones and that their higher stabilities are mainly due to less unfavourable entropy contributions since the enthalpy changes are much of similar magnitude. The results were explained in terms of a higher solvation of the primary amines in dmso compared with that of the secondary ones. Moreover a comparison between the thermodynamic functions of the silver(I) complexes in water and dmso indicates a higher solvation of the amines in the former solvent.

The nature of the solvent is therefore of paramount importance in the formation of complexes between chemical species in solution, since complex formation always occurs in competition with solvation of the species concerned.[2]

In order to obtain further insight into the solvent effect on complexation reactions this investigation has been extended to the interactions between silver(I) and other N-donor ligands of different bonding characteristics. We present here the results of equilibrium measurements on the interaction in dmso of silver(I) with a number of polyamines. The ligands investigated are 1,2-diaminoethane (en), 1,3-diaminopropane (tn), and diethylenetriamine (dien). Although these systems have been investigated in water[3–5] seemingly no such investigations in dmso have been reported, except for the silver(I)–en system.[6] As in the previous paper of this series, the measurements have been carried out at 25 °C and in a NEt_4ClO_4 medium of ionic strength 0.1 mol dm^{-3}.

Experimental

Chemicals.—All chemicals were commercial products of analytical grade. Silver perchlorate, $AgClO_4{\cdot}H_2O$ (Fluka), was dried under vacuum at 50 °C and used without further purification. The ligands were purified by fractional distillation.[7,8] Dimethyl sulphoxide and tetraethylammonium perchlorate were purified as described.[1]

The silver perchlorate solutions were prepared from anhydrous $AgClO_4$ and freshly distilled dmso. The exact silver content of the solutions was determined by potentiometric titration with chloride. Solutions of the ligands were prepared by dissolving known amounts of the amines in dmso and standardized by thermometric titration with standard $HClO_4$ solution. The ionic strength was maintained at 0.1 mol dm^{-3} with NEt_4ClO_4.

Potentiometric Measurements.—The galvanic cell and the potentiometric apparatus used were as described previously.[1] The potentiometric measurements were carried out by using a Radiometer PHM 84 equipped with a Metrohm EA 282/2 silver electrode as a working electrode and a Metrohm 440 silver electrode as a reference. Ingold vessels with outer jackets were used for the titrations. The temperature of the electrode solutions was kept at 25 + 0.1 °C by means of water circulating in the outer jackets. The procedure for the titrations was the same as before.[1] Titrations were carried out with at least three different initial silver(I) concentrations, c^0_M, ranging from 2.00 to 30.00 mmol dm^{-3}. All titrations were carried out in duplicate and in a few cases in triplicate. The electrode couple was periodically checked in the range $10^{-5} \leqslant [Ag^+] \leqslant 10^{-2}$ mol dm^{-3}. No significant deviations from Nernst's law were found. Other details were as previously reported.[1] The silver(I) complex-formation constants were calculated from the potentiometric data with use of the program SUPERQUAD.[9] The errors are expressed as three times the standard deviations.

Results and Discussion

The experimental data, for a few points chosen at random, plotted as $\bar{n}$, the average ligand number, *vs.* $-\log[L]$, where [L] is the concentration of the free ligand, are shown in Figure 1. The values of $\bar{n}$ and [L] were calculated, along with a preliminary graphical evaluation of the stability constants, according to a method proposed earlier.[10,11] The formation constants were then refined by means of the above mentioned least-squares program.[9] The stability constants are listed in the Table. For comparison, previously studied silver(I) complexes with the same ligands in aqueous solution are also included.

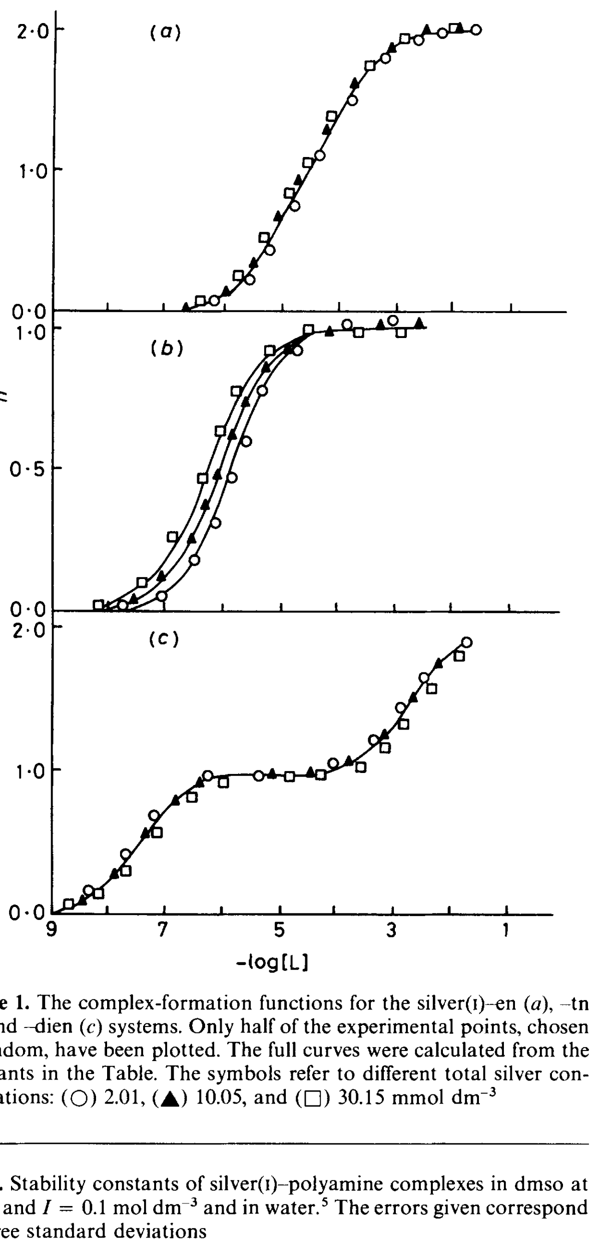

Figure 1. The complex-formation functions for the silver(I)–en (*a*), –tn (*b*), and –dien (*c*) systems. Only half of the experimental points, chosen at random, have been plotted. The full curves were calculated from the constants in the Table. The symbols refer to different total silver concentrations: (○) 2.01, (▲) 10.05, and (□) 30.15 mmol dm^{-3}

Table. Stability constants of silver(I)–polyamine complexes in dmso at 25 °C and I = 0.1 mol dm^{-3} and in water.[5] The errors given correspond to three standard deviations

Ligand	Reaction	log β_j	
		dmso	water[a]
en	$M + L \rightleftharpoons ML$	5.34(2)	4.70
	$M + 2L \rightleftharpoons ML_2$	9.50(3)	7.7
	$2M + L \rightleftharpoons M_2L$		6.5
	$2M + 2L \rightleftharpoons M_2L_2$		13.2
tn	$M + L \rightleftharpoons ML$	5.9(2)	5.85
	$2M + L \rightleftharpoons M_2L$	8.06(9)	6.45
	$2M + 2L \rightleftharpoons M_2L_2$	14.4(2)	15.9[b]
dien	$M + L \rightleftharpoons ML$	7.46(3)	6.1[c]
	$M + 2L \rightleftharpoons ML_2$	10.20(6)	
	$2M + L \rightleftharpoons M_2L$		7.5

[a] At 20 °C, I = 0.1 mol dm^{-3}. [b] At 25 °C, I = 3.0 mol dm^{-3}. [c] At 25 °C, I = 0.1 mol dm^{-3}.

The experimental data can be interpreted by the formation of two mononuclear complexes for the silver(I)–en and –dien systems. For Ag$^+$–tn, polynuclear species had also to be considered in addition to the mononuclear complex [Ag(tn)]$^+$: the best fit was achieved when the species [Ag$_2$(tn)]$^{2+}$ and [Ag$_2$(tn)$_2$]$^{2+}$ were taken into account.

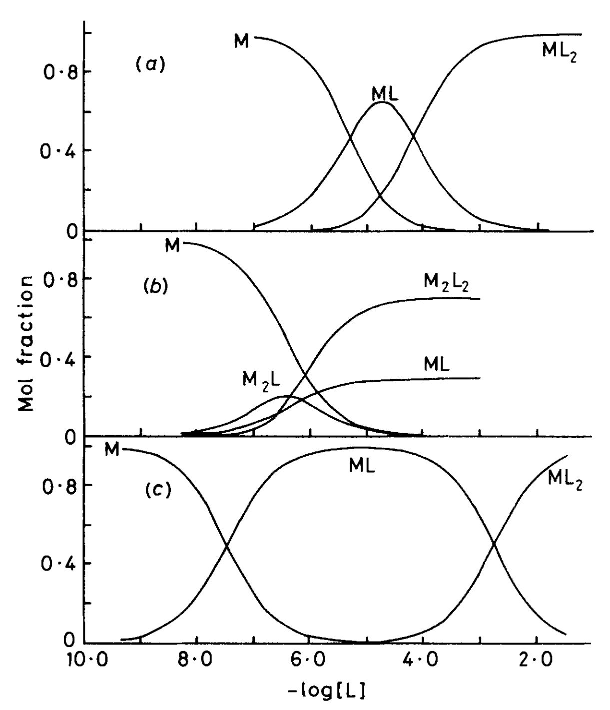

Figure 2. The distribution curves for the silver(I)–polyamine (see Figure 1) systems at c_M^0 = 10.0 mmol dm^{-3}

The silver(I)–1,2-diaminoethane system in dmso was investigated by Pool and Sandberg[6] who reported the formation of two mononuclear complexes, [Ag(en)]$^+$ and [Ag(en)$_2$]$^+$, and a polynuclear species [Ag$_2$(en)]$^{2+}$. The value of β_1 obtained here is somewhat lower than that found before (log β_1 = 6.27). Our value of β_2, on the other hand, agrees quite well with that reported by these authors (log β_2 = 9.54). On the contrary, there is no evidence, in the present study, of formation of polynuclear species. The complex-formation curve independent of c_M^0 (see Figure 1) confirms that no polynuclear species are formed in detectable amount. This is in accord with the fact that at the highest silver(I) concentration employed by Pool and Sandberg (c_M^0 = 33.0 mmol dm^{-3}) the distribution curves calculated from their stability constants show that the concentration of the polynuclear species [Ag$_2$(en)]$^{2+}$ is only a small fraction (less than 0.5%) of the total silver(I) concentration.

The distribution curves of the various silver(I) complexes are illustrated in Figure 2. In the system Ag$^+$–tn the complex [Ag$_2$(tn)]$^{2+}$ is the least stable and is formed at the beginning of the titration when the metal–ligand ratio is still very large; its concentration never exceeds 20% of the total silver concentration, whereas the dimeric species [Ag$_2$(tn)$_2$]$^{2+}$ is predominant throughout the range of free-ligand concentration investigated.

The formation constants of 1:1 complexes with the three ligands are all much larger than for the corresponding silver(I) complexes with unidentate monoamines, which suggests that the ligands all behave as chelating agents. The silver(I) complexes with tn are somewhat stronger than those with en, which is presumably due to some strain within the five-membered chelate ring formed by en as compared with the six-membered one formed by tn. The ratio K_1/K_2 for the silver(I) complexes with en is just above 1: this, along with the higher stability of [Ag(en)$_2$]$^+$ in comparison with those of 1:2 monoamine complexes, suggests that the second en also coordinates to the silver as a bidentate ligand.

The complex $[Ag(en)_2]^+$ has presumably a tetrahedral configuration. That of $[Ag(en)]^+$ may be either linear or slightly distorted tetrahedral: it is not easy to conclude, from free-energy data alone, whether a change in configuration from linear to tetrahedral occurs upon formation of the second complex. To decide this it would be very useful to know, in addition to the free-energy changes, also the enthalpy and entropy changes. A change in co-ordination is usually accompanied by abnormal values of the ratios K_j/K_{j+1}:[12] the ratio $K_1/K_2 = 1.3$ for this system suggests a tetrahedral configuration for the silver(I) complexes.

As mentioned above, the weaker complexes between silver and en relative to those with tn are likely due to formation of a strained chelate ring in $[Ag(en)]^+$. We would therefore expect formation of polynuclear species for this system, which indeed occurs in aqueous solution, rather than for the Ag^+–tn system. As seen from the Table, 1,2-diaminoethane does not form polynuclear complexes in dmso, but tn does. The more bulky nature and the longer methylene chain of tn seem to be responsible for this rather unexpected behaviour (see below).

As for the silver(I) complexes with en, also in this case it is not easy to draw any conclusion about the structure of the 1:1 complex $[Ag(tn)]^+$ in solution. The flexibility of the methylene chain of tn might favour a linear configuration.

Given the nature of the ligand, the stronger complexes between silver(I) and dien relative to the other ligands is probably to be ascribed to formation of two fused five-membered rings, with a tetrahedral configuration, the fourth position of the tetrahedron being occupied by a solvent molecule. As for the Ag^+–en system, no polynuclear complexes had to be accounted for: the complex-formation function indicates the formation of only two mononuclear complexes, $[Ag(dien)]^+$ and $[Ag(dien)_2]^+$. The very high value of the ratio $K_1/K_2 = 5 \times 10^4$ suggests that the second ligand does not act in a terdentate manner. Moreover the K_2 value for this system is close to those for silver(I) monoamine complexes.[1] It is therefore reasonable to believe that the second ligand molecule is unidentate.

The Table also lists the stability constants for the same systems in aqueous solution.[3–5] The values of the stability constants in water refer to experimental conditions similar to those adopted in the present investigation. In water a much larger number of species exists (see Table). Apart from the protonated species which cannot exist in dmso, in water polynuclear species have been ascertained for all the systems and also polymeric species for the Ag^+–en system.[13] In dmso only tn forms polynuclear complexes; for the other systems no polynuclear species could be detected, at least in appreciable amounts. This is presumably connected with the greater solvation of the amines in water, due to strong hydrogen bonds, which would make the amine groups less available for co-ordination to the same silver atom. Moreover the lower dielectric constant of dmso ($\varepsilon_{water} = 78.5, \varepsilon_{dmso} = 46.4$)[12] makes the electrostatic interactions stronger than in water and in this way counteracts the formation of species where two charged metal ions are close to each other: so en does not form polynuclear complexes, but tn does.

The different solvation of the amines in the two solvents is also responsible for the fact that, in spite of the exothermic enthalpy of transfer of Ag^+ from water to dmso,[14] the silver complexes with the ligands investigated here are stronger in dmso than in water (see Table). This phenomenon is not at all surprising as it had been observed for the complex formation between silver(I) and some monoamines.[1] The stronger solvation of the amines in water should compensate for the higher solvation of Ag^+ in dmso and, on the whole, make the silver(I) complexes with amines weaker in the former solvent.

A more detailed discussion will be postponed until the enthalpy and entropy contributions to the complex formation have become available.

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