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Solvent effect on the thermodynamics of Ag(I) coordination to tripodal polypyridine ligands

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Abstract An investigation on the thermodynamics of complex formation between Ag(I) ion and two tripodal ligands tris[(2-pyridyl)methyl]amine (TPA) and 6,6′-bis-[bis-(2-pyridylmethyl)aminomethyl]-2,2′-bipyridine (BTPA) has been carried out in the aprotic solvents dimethylsulfoxide (DMSO) and dimethylformamide (DMF) by means of potentiometry and titration calorimetry. The results for TPA are compared with those already obtained for other aliphatic tripodal polyamines. In general, the TPA ligand forms complexes less stable than 2,2′,2″-triaminotriethylamine (TREN) and tris(2-(methylamino)ethyl)amine (Me_3TREN) as a result of the combination of higher structural rigidity of TPA and lower σ-donor ability of pyridinic moieties with respect to primary and secondary amines. The same trend is found if the stability of Ag(I) complex with TPA is compared with that of tris(2-(dimethylamino)ethyl)amine (ME_6TREN), despite the pyridinic nitrogen is formally a tertiary one. Theoretical calculations run to explain the reasons of this weaker interaction indicate that this difference is due to solvation, rather than to steric or σ-donor effects. The ligand BTPA is able to form bimetallic species whose relative stability is largely influenced by the different solvation of Ag(I) ion in DMSO and DMF rather than by the difference in the dielectric constants of these two media.

Keywords Calorimetry · Non-aqueous solvents · Potentiometry · Silver(I) · Solvation · Thermodynamics

Introduction

In the last years, much interest has been paid to the thermodynamics of complex formation of metal ions with neutral linear and tripodal N-donors in water [1–4], as well as in non-aqueous [5–14] and mixed solvents [15]. The latter media can be considered simplified systems with respect to water, due to the absence of protonation equilibria and a lower degree of structural order, thereby a better understanding of metal–ligand interactions and the effects of solvent properties can be obtained.

The main aim of the fundamental thermodynamic works in this field is to investigate the influence of different basicity and steric properties of the ligands on the stability and nature of the complexes formed, for the design of selective complexation and recognition agents [4]. Moreover, the coordination chemistry of tripodal ligands with Group 11 metal ions in non-aqueous solvents has been subject of interest especially for the ability of their Cu(I) complexes to act as artificial mimics of natural oxygen carriers [16].

Many data are available also for the coordination of Ag(I) ion with monoamines, linear and tripodal polyamines and linear pyridine-based ligands in several media [3], but few are available for the coordination of tripodal polypyridines in water and organic solvents. Previous results in dimethylsulfoxide (DMSO) [17–19] have shown that the strength and the nature of the complexes formed with polyamines can be modulated through the degree of methylation present in the ligand, which influences their basicity, solvation, and steric hindrance.

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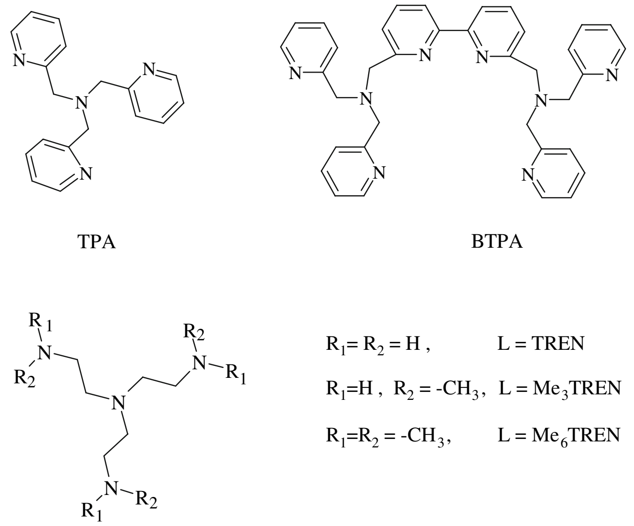
As an extension of our previous studies [17], we report the results of a thermodynamic investigation of the complex formation of Ag(I) with the tripodal ligands: tris[(2-pyridyl)methyl]amine (TPA) and 6,6′-bis-[bis-(2-pyridylmethyl)aminomethyl]-2,2′-bipyridine (BTPA) sketched in Scheme 1. The results have been obtained by means of potentiometry and titration calorimetry experiments, carried out in the aprotic solvents dimethylsulfoxide (DMSO) and N,N-dimethylformamide (DMF).

The main scope of this work is to study the effect of these two different solvents on the type and stability of Ag(I) species formed with these tripodal ligands. Furthermore, the determination of stability constants or Ag(I) in these media could be of practical utility for the thermodynamic study of other metal ions through competitive potentiometric titrations. This last technique has been widely employed to study lanthanides [20, 21], whose solution chemistry in organic solvents is important for assessing the selectivity of a ligand for liquid extraction applications. The results presented in this paper are also compared with those available in water for the same polypyridines and for similar *N*-methylated tripodal polyamines in DMSO (Scheme 1). Theoretical DFT (Density functional theory) calculations have been run to provide information about the relative stability of some complexes.

Experimental

Materials

Anhydrous silver perchlorate was obtained from $AgClO_4 \cdot H_2O$ (Fluka) as described previously [22]. The ligands TPA and BTPA were synthesized according to the procedures already reported [23, 24] and the purity checked by NMR and HPLC–MS analysis. The solvents, DMSO and DMF, and the background salt NEt_4ClO_4 were purified according to the described procedures [21, 25].



Scheme 1

Solutions of the ligands were prepared by dissolving weighted amounts in the anhydrous solvent. While TPA is rather soluble in both solvents, BTPA displays a much lower solubility in DMF and especially in DMSO (~ 2 mmol dm^{-3}): this is the main reason for the larger standard deviation for the complexation enthalpies in DMSO reported in Table 1. Solutions of $AgClO_4$ were prepared and standardized as before [22]. The ionic medium was adjusted to 0.1 mol dm^{-3} by means of appropriate amounts of NEt_4ClO_4 solutions. All the solutions were freshly prepared before each experiment in a glove-box under atmosphere of dry nitrogen. Their water content, typically 10 ppm, was determined by a Metrohm 684 KF Coulometer.

Potentiometry

All experiments were carried out in a thermostatic bath inside a glove box maintained at 298.0 ± 0.1 K. The experimental data required for the determination of the stability constants of the complexes were the equilibrium concentrations of the silver ion, which were obtained from the e.m.f. of a galvanic cell previously described [25]. The e.m.f. values were measured by means of an Amel 338 pH meter equipped with a silver working electrode and a Metrohm Ag/AgCl reference electrode. In the concentration range $10^{-6} < [Ag^+] < 10^{-2}$ mol dm^{-3}, the e.m.f. values varied with the metal ion concentration according to Nernst's law. A typical experimental run consisted in collecting equilibrium data points when solutions of silver perchlorate ($2 < C°_{Ag} < 10$ mmol dm^{-3}) were titrated with solutions of TPA $10 < C°_L < 70$ mmol dm^{-3} both in DMSO and DMF. In the case of BTPA, the concentrations used were $2 < C°_{Ag} < 10$ mmol dm^{-3} and $5 < C°_L < 20$ in DMF and $C°_L \sim 1.5$ mmol dm^{-3} in DMSO (in this last case $0.5 < C°_{Ag} < 1$ mmol dm^{-3}). Titrations were performed with at least three different initial Ag(I) concentrations and some of them were carried out in duplicate to verify the reproducibility of the system. The Hyperquad [26] program was used for the calculation of the stability constants. Speciation calculations and plots have been made with the EST tool for MS-Excel [27].

Titration calorimetry

A Tronac model 87-558 isoperibol titration calorimeter equipped with a 25 mL vessel was used to measure the heats of reactions. The cover of the titration vessel and its connection to the calorimeter were modified in order to

Table 1 The overall stability constants and corresponding thermodynamic parameters for the reactions $i\text{Ag} + j\text{L} \leftrightarrows \text{Ag}_i\text{L}_j$ in DMSO and DMF; $T = 298$ K

L	Ag_iL_j	log β_{ij}	$-\Delta G°_{ij}$ / kJ mol^{-1}	$-\Delta H°_{ij}$ / kJ mol^{-1}	$-T\Delta S°_{ij}$ / kJ mol^{-1}
DMSO					
TPA	AgL	5.89 (0.01)	33.6 (0.01)	46.1 (0.5)	12.5
	AgL_2	7.29 (0.03)	41.6 (0.2)	84.7 (0.8)	43.1
BTPA	AgL	8.40 (0.04)	47.9 (0.2)	62 (1)	14.1
	Ag_2L	12.71 (0.05)	72.4 (0.3)	112 (3)	39.6
DMF					
TPA	AgL	8.26 (0.01)	47.2 (0.1)	64 (1)	16.8
	AgL_2	10.40 (0.01)	59.4 (0.1)	88 (3)	28.6
BTPA	AgL	11.44 (0.04)	65.2 (0.2)	73 (1)	8.8
	Ag_2L	18.52 (0.05)	105.6 (0.3)	129 (2)	23.4
	AgL_2	13.9 (0.1)	79.3 (0.5)	115 (2)	35.7

The error limits represent 3σ

ensure the reactions proceed in an inert atmosphere. Both the vessel and the burette were filled and joined together inside the glove-box, taken out and connected to the calorimeter for measurements. The experimental value of the heat of neutralization of tris(hydroxymethyl)methylamine (THAM) with 0.1 mol dm^{-3} HCl was found to be $\Delta H° = -47.59$ kJ mol^{-1}, in good agreement with the accepted value of -47.53 ± 0.13 kJ mol^{-1} [1]. The calorimetric titrations were performed at 298.00 ± 0.02 K by adding at constant rate known volumes of ligand solutions ($10 < C°_{\text{TPA}} < 60$ mmol dm^{-3}) to 20 mL of Ag^+ solutions ($1 < C°_{\text{Ag}} < 10$ mmol dm^{-3}). In the case of the Ag/BTPA system in DMSO, reversed calorimetric titrations (i.e., a ligand solution in the cell titrated with an Ag^+ solution in the burette) were run, due to the low solubility of this ligand in this solvent. Typically, the concentrations were $0.7 < C°_{\text{BTPA}} < 1.5$ mmol dm^{-3} titrated with a solution with $8 < C°_{\text{Ag}} < 20$ mmol dm^{-3}).

For each metal/ligand system, usually 3–4 titration runs with different $C°_{\text{Ag}}$ were performed to achieve better statistics in the calculation of formation constants and reaction enthalpies. The heat of dilution of Ag(I) ion and ligands solutions were also determined. The standard molar enthalpy of formation for the metal complexes, were calculated by using the computer program HyperDeltaH [28].

Computational details

Density functional theory calculations were performed on the $\text{Ag(Me}_6\text{TREN)}^+$ and Ag(TPA)^+ complexes. The three-parameter hybrid functional B3LYP [29, 30] has been employed for these calculations as implemented in the software GAMESS-US [31] using the SBKJC ECP [32] basis set for Ag(I) and a triple-ζ basis set for the other elements. The structures of the complexes were optimized within the C_3 symmetry group and the vibrational analysis was performed to check that they were effectively minimum structures. Solvational effects have been introduced using the C-PCM model [33] with the GAMESS-US internal parameters for DMSO. The energy in solution has been obtained by performing a single point calculation on the gas-phase optimized structures. Preliminary calculations indicated that the correction for the basis set superposition error (BSSE) to the binding energy was negligible and therefore not applied.

Results and discussion

The analysis of the potentiometric data for TPA and BTPA gives the values of the stability constants reported in Table 1. Mononuclear AgLj species ($j = 1, 2$) are formed by TPA in both solvents, whereas BTPA forms the additional binuclear Ag_2L complex.

The potentiometric titration curves in both solvents are reported for BTPA in Fig. 1a and b in the form of Δe.m.f. (the difference between the e.m.f. measured at each point and the initial value read before adding the ligand to the AgClO_4 solution) versus $R_c = C_{\text{L}}/C_{\text{M}}$, superimposed with the species distribution relative to the metal ion. From the shape of the titration curves, the formation of the binuclear Ag_2L species is easily foreseen and in DMF this is almost the only existing species at $R_c = 0.5$.

The calorimetric curves, in form of total enthalpy of reaction per mole of Ag(I) ion (Δh_v) vs. R_c, are displayed in Figs. 2 and 3 for the two ligands in DMSO and DMF, respectively. A clear change of slope is present at $R_c = 0.5$ for BTPA systems in DMSO and in DMF, thus confirming the presence of a stable binuclear complex. The heat evolution after $R_c = 1$ for TPA system in both solvents indicates the presence of a low stability AgL_2 complex, as resulting also from the treatment of experimental data. Additional heat is evolved after $R_c = 0.5$ both in DMSO and in DMF also in the case of Ag/BTPA systems, due to

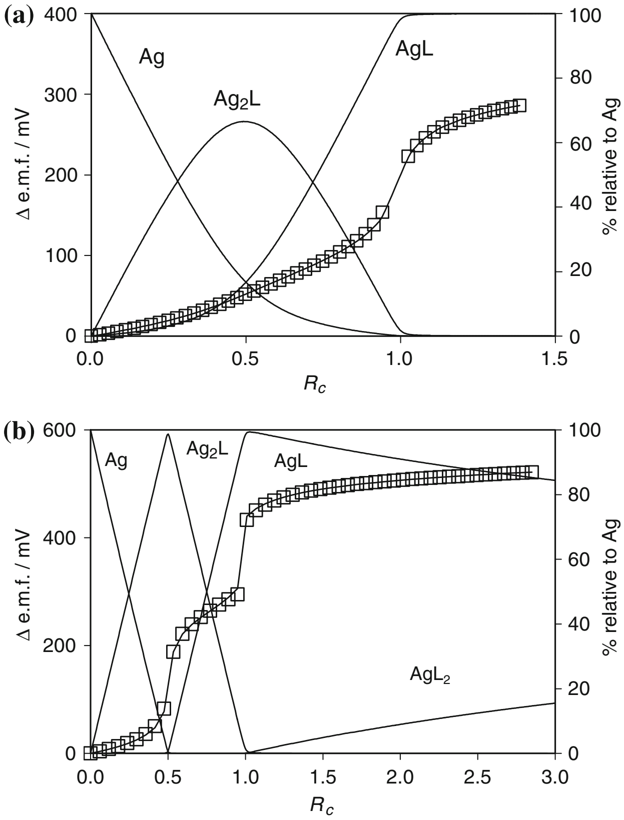


Fig. 1 Plot of the observed and calculated Δ e.m.f. values for two titrations of Ag(I) solutions with BTPA solutions: **a** $C°_{Ag} = 0.7$ mmol dm^{-3}, $C°_{BTPA} = 1.4$ mmol dm^{-3} in DMSO; **b** $C°_{Ag} = 1.2$ mmol dm^{-3}, $C°_{BTPA} = 10.1$ mmol dm^{-3} in DMF. The speciation plots are also reported

the formation of AgL (in DMSO) and AgL_j (j = 1, 2 in DMF) species. In particular, in DMF the stepwise log K values for the reactions $Ag_2L + L \leftrightarrows 2AgL$ and $AgL + L \leftrightarrows AgL_2$ are 4.36 and 2.46, respectively, the formation of the latter complex is therefore not complete even at high R_c ratios, as clearly evidenced in the distribution diagram in Fig. 1b.

The values of the standard Gibbs free energy of complexation, along with the corresponding enthalpy and entropy values, are reported in Table 1. In all cases, the reactions are enthalpy only driven, since the entropic values oppose to complex formation. This is an usual feature of complex formation of Ag(I) ion in aprotic solvents with neutral ligands, where the loss of entropy of the reagents is not compensated by desolvation process [3].

DMSO solutions

The values of thermodynamic parameters for 1:1 complex formation indicate that the TPA ligand is fully coordinated to the metal ion. A comparison can be made with the parent linear ligand bis-(2-pyridyl)methyl)-amine (DPA), whose thermodynamic parameters were previously [34] determined in DMSO ($\log\beta_{11} = 4.37$ and $\Delta H°_{11} = -37.7$ kJ mol^{-1}) and which has been proved to be completely bound to silver by means of NMR and FT-IR spectroscopy [34]. The AgL_2 species is relatively weak: the high value of K_1/K_2 ratio ($\sim 10^4$) suggests a rearrangement of the coordination sphere around Ag(I) ion in the second complexation step. The associated rather unfavorable value

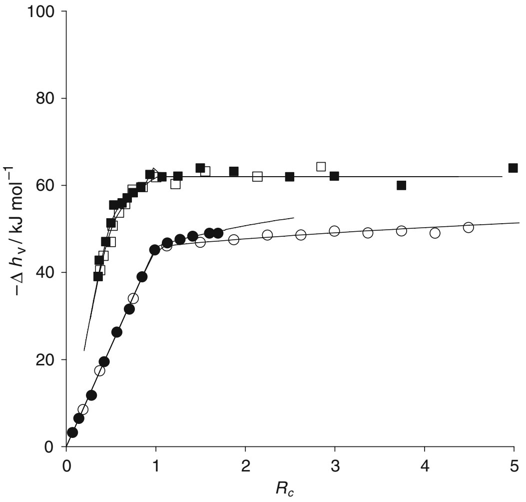


Fig. 2 Total molar enthalpy changes per mole of Ag, Δh_v, as a function of the ligand to metal ratio $R_c = C_L/C_{Ag}$ in DMSO for: **a** Ag–TPA system: (*open circle*) $C°_{Ag} = 2.1$ mmol dm^{-3}; (*filled circle*) $C°_{Ag} = 8.4$ mmol dm^{-3}; **b** Ag–BTPA system (reversed titration): (*open square*) $C°_L = 0.7$ mmol dm^{-3}; (*filled square*) $C°_L = 1.5$ mmol dm^{-3} titrated with $C°_{Ag} = 10.3$ and 19.8 mmol dm^{-3}, respectively. Only some of the experimental points are displayed

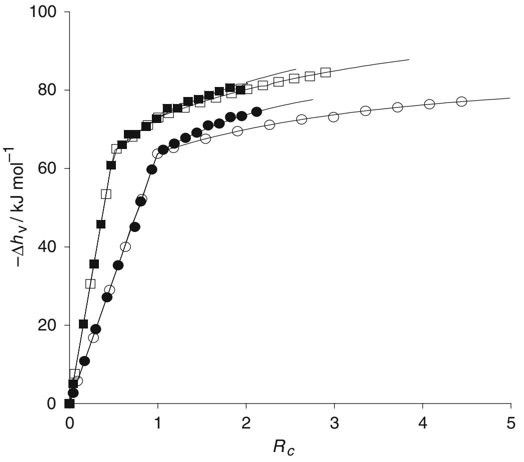


Fig. 3 Total molar enthalpy changes per mole of Ag, Δh_v, as a function of the ligand to metal ratio $R_c = C_L/C_{Ag}$ in DMF for: **a** Ag–TPA system: (*open circle*) $C°_{Ag} = 2.6$ mmol dm^{-3}; (*filled circle*) $C°_{Ag} = 8.5$ mmol dm^{-3}; **b** Ag–BTPA system: (*open square*) $C°_{Ag} = 1.0$ mmol dm^{-3}; (*filled square*) $C°_{Ag}$ 3.1 = mmol dm^{-3}. Only some of the experimental points are displayed

of stepwise $T\Delta S°_{12}$ is indicative that the metal desolvation is nearly complete at the first complexation step in DMSO.

The values of $\log\beta_{11}$ and $\Delta H°_{11}$ are lower in magnitude than those found in DMSO [17, 25] for tripodal polyamines 2,2′,2″-triaminotriethylamine (TREN), tris(2-(methylamino) ethyl)amine (Me_3TREN) and tris(2-(dimethylamino)ethyl) amine (ME_6TREN) in Scheme 1 (see Table 2). The higher stability of the Ag(I)-TREN and Ag(I)-Me_3TREN complexes is easily explained by their stabilization due to H-bonding with the surrounding DMSO molecules (also evident from the very negative entropy of complexation in Table 2) and by the higher basicity of the primary and secondary amine in solution with respect to pyridine [3].

The comparison with Me_6TREN is interesting, since the pyridine nitrogen of TPA is formally tertiary and therefore such destabilization of TPA complexes with respect to Me_6TREN ones was not expected. Several arguments can be invoked to explain such different $\Delta G°$ and $\Delta H°$ values and to this purpose DFT calculations have been performed to compute the binding energies relative to the formation of $Ag(Me_6TREN)^+$ and $Ag(TPA)^+$ complexes (Table 3). The results from the DFT calculations attribute the preferential interaction of Me_6TREN with Ag(I) to a dominant solvational effect. In fact, the difference of binding energy ($\Delta E_{bind} = E_{bind}(Ag(TPA)^+) - E_{bind}(Ag(Me_6TREN)^+)$) is slightly negative in vacuum (i.e., TPA coordination favored) indicating that the contribution of the σ-bonding and steric strain of the two ligands is similar. On the contrary, a largely positive ΔE_{bind} is found when introducing the solvent effect.

The formation of a second AgL_2 species for TPA, as well as observed for the other tripodal ligands in Table 2, is a special feature of these non-aqueous solutions as in water only the AgL species is observed. The thermodynamic parameters found in water by Anderegg et al. [35] at 293.15 K and I = 0.1 M (KNO_3) are: $\log\beta_{11} = 7.92$, $\Delta G°_{11} = -44.4$ kJ mol^{-1}, $\Delta H°_{11} = -68.6$ kJ mol^{-1}, $T\Delta S°_{11} = -24.2$ kJ mol^{-1}. The less favorable $\Delta H°_{11}$ value in DMSO is evidently due to the stronger solvation of Ag(I) ion in this solvent and can be predicted by considering the largely negative transfer functions from water to DMSO [3]. The less favorable entropy of complex formation in water with respect to DMSO may be explained with a higher solvation of the final complex in the former solvent.

Table 3 Binding energies E_{bind} (kJ mol^{-1}) of Me_6TREN and TPA with Ag^+ in vacuum and DMSO

Complex formed	E_{bind} Vacuum	E_{bind} DMSO
$Ag(Me_6TREN)^+$	−491.8	−314.2
$Ag(TPA)^+$	−498.2	−272.7
ΔE_{bind}	−6.4	+41.5

The value of $\log\beta_{11}$ for BTPA is higher (2.51 log units) than that found for TPA, essentially for the more negative $\Delta H°_{11.}$ In addition, its stability is even higher than that displayed by the tertiary Me_6TREN and is especially entropy driven in comparison with this latter ligand. Several explanations can be tentatively proposed to interpret the thermodynamic results.

Silver(I) can be 5 or even 6 coordinated in solid state with pyridine donor ligands (see for example Refs. [36, 37]): taking into account this possibility also in solution, the change from the tetrahedral geometry present in $AgClO_4$ solvate in DMSO [38] should result in a markedly less negative $\Delta S°$ with respect to TPA coordination, which does not seem to occur in this case. On the other hand, the encapsulation of Ag(I) should "lock" the BTPA with a consequent loss of many degrees of freedom of this large and flexible ligand which compensates desolvation with a negative conformational entropy contribution. An alternative hypothesis should be that the coordination mode with BTPA is different than with TPA, involving two monopyridinic units and two tertiary nitrogens bonded to Ag(I), leading to a decrease in the steric strain of the resulting species.

The main feature of BTPA ligand with respect to TPA is the formation of the bimetallic Ag_2L complex. The

Table 2 Thermodynamic parameters for the formation of Ag(I) complexes with tripodal polyamines in DMSO at T = 298 K taken from refs. [17, 25]

L	Ag_iL_j	Log β_{ij}	$-\Delta G°_{ij}$ / kJ mol^{-1}	$-\Delta H°_{ij}$ / kJ mol^{-1}	$-T\Delta S°_{ij}$ / kJ mol^{-1}
TREN[25]	AgL	9.49	54.1	90	35.9
	AgL_2	11.10	63.3	102	38.7
	Ag_2L	11.51	65.6	97	31.4
Me_3TREN[17]	AgL	8.68	49.5	83.0	33.5
	AgL_2	9.88	56.4	100	43.6
	Ag_2L	9.69	55.3	98	42.7
Me_6TREN[17]	AgL	7.63	43.6	73.8	30.2
	AgL_2	9.06	51.4	90	38.6
	Ag_2L	9.75	55.8	100	44.2

presence of several donating groups (BTPA is essentially made up of two TPA units) at relatively high distances clearly allows the formation of this last species since the repulsion between the positive charge of the ions is minimized. Several examples of crystal structures of these bimetallic complexes with BTPA are available in literature and report Metal–Metal distances ranging from 4.9 to 8.0 Å [24, 39, 40].

DMF solutions

This solvent has some differences with respect to DMSO, mainly in the values of dielectric constant ($\varepsilon(\mathrm{DMSO}) = 46.45$, $\varepsilon(\mathrm{DMF}) = 36.71$) [41] and, to a lesser extent, in the donor number ($\mathrm{DN(DMSO)} = 29.8$, $\mathrm{DN(DMF)} = 26.6$) [41]. Nevertheless, it is difficult to make predictions on the nature and stability of the complexes formed by Ag^+ with these ligands on the basis of these parameters only.

In DMF, the Ag(I) ion forms with TPA and BTPA 1:1 complexes characterized by ΔG° and ΔH° values more negative than those found in DMSO. This result can be explained with the thermodynamic parameters of transfer from DMF to DMSO for the Ag(I) ion, calculated on the basis of the data in literature at 298 K [42]: $\Delta G°_{tr}(\mathrm{DMF} \rightarrow \mathrm{DMSO}) = -14.7$ kJ mol^{-1} and $\Delta H°_{tr}$ $(\mathrm{DMF} \rightarrow \mathrm{DMSO}) = -10.2$ kJ mol^{-1} $T\Delta S°_{tr}$ $(\mathrm{DMF} \rightarrow \mathrm{DMSO}) = +4.5$ kJ mol^{-1}. Clearly, the stronger solvation of Ag(I) ion in DMSO is the main responsible of the higher stability of the species formed in DMF. This hypothesis is also confirmed by the fact that difference between the stability in the two solvents ($\Delta\log\beta_{11,\mathrm{TPA}}(\mathrm{DMF} \rightarrow \mathrm{DMSO}) = 2.4$ and $\Delta\log\beta_{11,\mathrm{BTPA}}(\mathrm{DMF} \rightarrow \mathrm{DMSO}) = 2.7$) is of the same order of magnitude as that found for a linear tridentate diethylenetriamine (DIEN) [21] $\Delta\log\beta_{11,\mathrm{DIEN}}(\mathrm{DMF} \rightarrow \mathrm{DMSO}) = 2.7$. Given the fact that Ag(I) ion is tetrahedrally solvated both in DMSO and DMF [38], the trend of thermodynamic parameters in both solvents suggests retention of this structure also in DMF, with the ligands coordinated through four donor atoms.

In DMF, the Ag(I) ions is able to form with BTPA an additional stable Ag_2L complex. If the values in Table 1 are considered, it can be noted that the relative Ag_2L/AgL stability is much higher than in DMSO. On the basis of the values of the dielectric constants, one should foresee that in the case of formation of polynuclear species the electrostatic repulsion between metal ions close to each other should be stronger in DMF than in DMSO. The opposite result indicates that the coordination sites are at a distance for which repulsion between the positive charge of the two coordinated metal ions is not important.

On the other hand, this large difference in stability is difficult to be explained by taking into account the small difference in DN values only, which give a qualitative indication of the donor ability of the solvent. In the case of Ag(I), this lower donor ability of DMF with respect to DMSO is reflected in the significant differences in the transfer thermodynamic parameters (see above). As a matter of fact, it can be observed that the ΔG° values for the reaction $AgL + Ag \leftrightarrows Ag_2L$ are −40.4 and −24.5 kJ mol^{-1} in DMF and DMSO, respectively, showing that the extra-gain in ΔG° in DMF (−15.9 kJ mol^{-1}) is strictly related to $\Delta G°_{tr}$ (DMF → DMSO; −14.7 kJ mol^{-1}).

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