# Thermodynamics of Complex formation of Silver(I) with N-Donor ligands in non-aqueous solvents.

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**Abstract.**

The results of a potentiometric and calorimetric study on the complexation reactions of neutral N donor ligands with silver(I) in propylenecarbonate (PC) and dimethylformamide (DMF) are reported.

The ligands concerned in DMF are butylamine (*n*-but), 1,2-diaminoethane (EN), bis(2-aminoethyl)amine (DIEN) and *N,N'*-bis(2-aminoethyl)ethane-1,2-diamine (TRIEN) whereas in PC results are provided for EN and DIEN, because of side reactions occurring for n-but and TRIEN. The data are compared to those previously reported in dimethylsulfoxide (DMSO), acetonitrile (AN) and water, solvent media which present quite different dielectric constants ($\varepsilon$) and donor numbers (Dn). The trend of stabilities of the mononuclear AgL and $AgL_2$ formed is discussed in term of different cation and amines solvation in the different solvents. TRIEN can form bimetallic species in DMF, but not in DMSO. Given the lower $\varepsilon$ value for DMF than for DMSO, $Ag_2TRIEN$ formation is evidently more influenced by the lower solvation of Ag(I) ion in DMF, rather than by difference in dielectric constants of these two solvents. In PC in addition to mononuclear complexes of higher stability with respect to the former solvents, also polynuclear $Ag_2L$ and $Ag_3L_2$ species are found.

**Keywords**: Silver(I), amines, complexes, water, non aqueous solvents, thermodynamics, calorimetry

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## 1. Introduction.

In the last decades many studies have been carried out in the field of the thermodynamics of metal complex formation with nitrogen-donor (N-donor) ligands in water[1–4] as well as in non-aqueous or mixed solvents[5–13]. The main aim of these works has been to investigate the influence both of different basicity and steric properties of the ligands and of the solvents on the stability and nature of the complexes formed. All these studies are of great importance to understand or predict the role of metal ions in biological systems[14] and medicine, where for instance, an accurate description of the thermodynamics of complex formation is of capital importance in the design either of metal sequestering drugs [15,16] and diagnostic agents[17–19]. Also interesting structure-stability relationships have been derived when complexes with N-donor ligands are employed as small-molecule carriers [9,10,12,20–24] or in homogeneous catalysis when N-N, N-P or N-S chelating ligands were concerned [25,26].

In environmental applications, stability constants are essential pieces of information to predict the behavior and speciation of metals [27] as well as to design selective and efficient separative methods. As far as metal extraction from aqueous media is concerned, thermodynamic data for complex formation in organic media are useful for the design of ligands suitable for a separation of specific ions from the aqueous phase. In addition, thermodynamic data in aprotic organic solvents provided fundamental information on the effect of solvation on complex formation and on the metal-ligand interactions, as these solvents are simplified systems with respect to water and provide a better understanding of metal-ligand interactions.

Many thermodynamic studies have been carried out for the coordination of Ag(I), Co(II), Cd(II) and block-$f$ ions with polydentate amines, mostly in dimethylsulfoxide (DMSO) [5,7,10,12,13,22–24,26,28–35] and acetonitrile (AN) [36–40]. A considerable number of different ligand structures have been studied in these works and the results showed that the strength and nature of the complexes formed were largely influenced by ligands structures and donor-atom basicity and steric properties. On the other hand, less attention has been paid to these metal-amines systems in other organic media [5,6,41–43].

As an extension of previous works, we report here the results of a potentiometric and calorimetric study on the complexation reactions of neutral N-donors, butylamine ($n$-but), 1,2-diaminoethane (EN), bis(2-aminoethyl)amine (DIEN) and $N,N'$-bis(2-aminoethyl)ethane-1,2-diamine (TRIEN), with silver(I) in propylenecarbonate (PC) and dimethylformamide (DMF). These aprotic solvents are characterized by dielectric constants ($\varepsilon$) and donor numbers (Dn) ($\varepsilon = 36.71$ and $64.92$; Dn $= 26.6$ and $15.1$ for DMF and PC respectively) which are markedly different from water ($\varepsilon = 78.36$;

Dn = 18) and DMSO ($\varepsilon = 46.45$; Dn = 29.8) [44], where many previous works on Ag(I)-amine complexation have been carried out. Besides the interest on the solvent effect, stability data on Ag(I) in these media is of practical utility for the thermodynamic study of other metal ions through competitive potentiometric titrations [45].

## 2. Experimental

### 2.1 Materials

Anhydrous silver perchlorate was obtained from $AgClO_4 \cdot H_2O$ (Fluka) and treated as described previously[29]. The ligands (Aldrich, >98%) were purified by fractional distillation. DMF and PC (Fluka > 99%) and the background salt $NEt_4ClO_4$, used to maintain the required 0.1 M ionic strength were purified according to the described procedures[26,43].

Solutions of the ligands were prepared by dissolving weighted amounts in the anhydrous solvents. All the solutions were prepared afresh before each experiment in a MB Braun glove box under atmosphere of dry nitrogen. The water content in the solutions, typically 5-10 ppm, was determined by a Metrohm 684 KF Coulometer.

### 2.2 FT-IR Spectroscopy

To check stability of the ligands in PC silver(I) solutions, FT-IR spectra were recorded by means of a Bruker Vector 22 FT-IR spectrometer on KBr pellets. The concentration of the amines was varied between 30 and 100 $mmol^{-1}\ dm^{-3}$.

### 2.3. Potentiometry

All measurements were carried out inside the MB-150 MBraun glove box in a thermostated galvanic cell maintained at $298.1 \pm 0.1$ K. Ag(I) ion equilibrium concentrations, obtained from the e.m.f. of the cell, were used for the determination of the stability constants of the complexes. The emf were measured by means of an Amel 338 pHmeter equipped with a silver Metrohm 6.1248.010 electrode as a working electrode and a Metrohm 6.0718.000 silver electrode as a reference. An experimental run consisted in collecting equilibrium data points when solutions of silver perchlorate ($2.00 < C^\circ_{Ag} < 30.0$ mmol $dm^{-3}$ in DMF and $2.00 < C^\circ_{Ag} < 20.0$ mmol $dm^{-3}$ in PC) were titrated with solutions of the ligands ($50 < C^\circ_L < 200$ mmol $dm^{-3}$ in DMF and $30 < C^\circ_L < 100$ mmol $dm^{-3}$ in PC). Titrations were performed with at least three different initial Ag(I) concentrations and some titrations were

carried out in duplicate to verify the reproducibility of the system. In the concentration range $10^{-6} <$ $[Ag^+] < 10^{-2}$ mol dm$^{-3}$, the emf values varied with the metal ion concentration according to Nernst's law.

The computer program Hyperquad[46] was used for the calculation of the stability constants and Solverstat and EST tools[47,48] for statistical analysis and speciation calculations.

## 2.4. Calorimetry

A Tronac model 87-558 precision calorimeter was employed to measure the heats of reaction. The calorimeter was checked by titration of tris(hydroxymethyl)aminomethane (tham) with a standard solution of HCl in water. The experimental value of the heat of neutralization of tham was found to be $\Delta H° = -47.61$ kJ mol$^{-1}$, in good agreement with the accepted value of $-47.53 \pm 0.13$ kJ mol$^{-1}$ [49]. The calorimetric titrations were performed at $298.15 \pm 0.02$ K by adding known volumes of ligand solutions using similar ligand and Ag(I) concentration ranges as in potentiometry. The heats of dilution of the reactants, determined in separate runs, were found negligible. The least squares computer program HypDeltaH[50] was used for the calculation of the standard formation enthalpies.

## 3. Results

Reaction of propylene carbonate with amines to give carbammates could not be excluded in the time frame of both calorimetric and potentiometric experiments, being the reaction rate dependent on various factors such as nucleophilicity, structure, and steric hindrance of the selected ligands[51]. So the stability of the amines in PC was preliminary monitored by collecting, at different times, FT-IR spectra of 100 mM solutions of the ligands to detect possible changes in the absorptions of the N-H stretching modes, at ~3250, $\nu_{sym}$, and 3330 cm$^{-1}$, $\nu_{asym}$, of the free amine. Unfortunately, in the case of $n$-but and TRIEN solutions, the intensities of the peaks decreased noticeably within about 80 minutes (~100 min when the amine concentration was decreased to 30 mM) whereas the spectra did not change at least for the first 150 minutes when EN and DIEN were considered. Therefore, only the latter amine-Ag(I) systems were successfully studied in PC.

In Table 1, the overall stability constants and thermodynamic data for silver(I)- amine systems, with the limits of error indicated, are listed for the reactions: $i\text{Ag}^+ + j\text{L} \rightleftharpoons \text{Ag}_i\text{L}_j^+$ ($i = 1, 2$ $j = 1, 2, 3$; L is the ligand considered) in DMF and PC. In the same Table also the available thermodynamic data for silver complex formation with the same amines in water[1], DMSO[29,31,32] and AN[40] have been entered.

The best fit of potentiometric data is obtained when two mononuclear species AgL and $\text{AgL}_2$ are considered for all the ligands in DMF but tetradentate TRIEN, which forms only AgL and the dinuclear complex $\text{Ag}_2\text{L}$ (Fig. 1, Table 1).

For DIEN in PC, in addition to AgL and $\text{AgL}_2$, two polynuclear, $\text{Ag}_2\text{L}$ and $\text{Ag}_3\text{L}_2$, species were also detected, whereas no evidence of a better fit of the data was attained considering the additional presence of $\text{Ag}_2\text{L}_2$ complexes, as previously observed with some other methylenic and ethylenic P-N donors in PC [26]. Noteworthy, $\text{Ag}_3\text{L}_2$ species were also found in PC in the case of some more complex diaza ligands[52].

In Fig. 1 some potentiometric titration curves for Ag(I) with DIEN in PC (Fig.1a) and with TRIEN (Fig.1b) in DMF, are shown as the most significant ones. The sharp inflexion point at $R_C$ ($= C_L/C_M$) $= 0.67$ (Fig.1a) is indicative of the formation of the $\text{Ag}_3\text{DIEN}_2$ in PC. In Fig. 1 (inset) the speciation of Ag(I) as a function of $R_C$ is plotted for the two systems for $C^\circ_{\text{Ag}} = 10$ mmol dm$^{-3}$. In DMF $\text{Ag}_2\text{TRIEN}$ reaches a maximum value of 24% when $C^\circ_{\text{Ag}}$ is 30 mmol dm$^{-3}$ and its introduction is always required to obtain a good fit of the potentiometric data. In PC $\text{Ag}_2\text{DIEN}$ and $\text{Ag}_3\text{DIEN}_2$ species reach up to 11 and 28 %, respectively, of the silver distribution when $C^\circ_{\text{Ag}} = 20$ mmol dm$^{-3}$.

The calorimetric titration data points and related calculated curves (obtained with stability constants and enthalpy values reported in Table 1), for the same systems as Fig. 1, are reported in Fig. 2, as $\Delta h_v$, the total heats of reaction per mole of metal ion, $vs.$ $R_C$. From an examination of the shape of these curves some conclusions can be drawn about the prevalent complex species formed in solution. In the case of the Ag(I)-DIEN system in PC, the change of the slope occurring at $R_C = 0.5$ (Fig. 2a) and the slight differentiation of the curves till $R_C = 1$ confirm the presence of the previous described polynuclear species and show the importance of calorimetric results in monitoring the nature of the formed species, i.e. $\text{Ag}_2\text{L}$ and $\text{Ag}_3\text{L}_2$. For TRIEN in DMF, a splitting in the curves at different concentrations is present till $R_C = 1$ and no heat is evolved after this value (Fig. 2b), a clear indication that additional species are not formed after AgL.

# 4. Discussion.

The structure of the solvated Ag(I) ion in all the solvents considered (except PC, for which no data are available) is tetrahedral[53–55], thus the comparison of the transfer properties can be used profitably to discuss the energetics of desolvation of the metal ion upon complexation. The available transfer functions for Ag(I) from AN, considered as reference, to the solvents of concern[56] are presented in Table 2, together with acceptor (An) and donor number (Dn) values[44]. The Gibbs free energy of transfer in Table 2 show the following order of affinity of silver(I) for the different solvents: DMSO > AN > DMF > water > PC. So, as far as only the pivotal silver(I) solvation strength is considered, a decrease in the stability of metal-amine complexes on going from water to DMF, AN and DMSO and an increase of stability on going from water to PC is expected. The heat of solvation results more negative in the aprotic solvent DMSO than in the protic solvent such as water. This reflects the higher energy required to break the strong hydrogen bonds of the water structure than to disrupt the structure of liquid DMSO. In addition, the soft Ag(I) slightly prefers DMSO to AN and disregards PC.

It is to notice a peculiarity of the silver(I) with respect to other univalent cations: AN and PC donor numbers (Table 2) [44] would suggest a high degree of similarity in their interactions with silver(I) in sharp contrast to the large free energy of transfer $\Delta G°_{tr(AN \rightarrow PC)}$ (Table 2) [56]. For other monovalent cations, such as alkaline ones or $Tl^+$, the observed free energies of transfer are close to zero or very small. Even if there is a lack of information about the geometry of silver(I)/PC solvate, one can argue that this singular behaviour could be related to the peculiar solvation of silver(I) by acetonitrile which is σ-bonded by donating electron pairs in the π-orbitals to four $dsp^2$ hybrid orbitals on the $Ag^+$ ion. The coordinate bond seems to be strengthened by back-donation of nonbonding $4d_{z,x}$ and $4d_{y,z}$ electrons and this is presumably also the main reason why $Ag^+$ ion is preferentially solvated by acetonitrile also in acetonitrile/water mixture.(x Andrea : inserire ref. con numero 57 e shiftare le altre)

All the Ag(I) complexes are formed in strongly exothermic reactions whereas the entropy terms are negative (Table 1) as typically found for reactions involving complexation of metal ions by neutral ligands in aprotic solvents[5–8,12,23,41,57,58]. The negative entropy values are in line with the fact that the release of solvent molecules from the coordination sphere of the metal ions, does not compensate the decrease in conformational and translational entropy of the ligand.

A first glance to the thermodynamic data in Table 1 clearly indicates that the stability order for the Ag(I) mono- and poly-amine complexes in the different solvents increases in the order: water < DMSO < AN < DMF < PC. This trend reflects the prevailing of metal ion solvation effects (see above) on the complexation; the discrepancy observed for water can be explained as due to a strong

solvation, *via* hydrogen bonds, of primary and secondary polyamines in this solvent[6]. This hypothesis is also confirmed by literature data showing that when Ag(I) forms complexes with ligands which are H-bond acceptors only, like pyridines[59] or tertiary amines[8,11], the metal ion solvation prevails and the trend of stability in water and DMSO is reversed. Moreover, similar behaviours in complexation of amines were observed for other metal cations, namely Cd(II) and Co(II), whose solvation is larger in DMSO than in water [7,8,10,13,58].

The solvation of the amines considered in this study is decreasing, with respect to water and DMSO, in DMF and PC and this produces an increased stability of the complexes, in agreement with prevailing metal ion solvation effect.

Some common features can be noticed in the comparison of the results obtained in PC and DMF. In the case of *n*-but the first stepwise formation constant, $K_{11}$, is equal to the second one, $K_{12}$, and this is not in line with partial charge neutralization and increased steric hindrance which are normally factors decreasing the stability of successive species. The same results has been observed in the other solvents and explained previously in the case of water [6,60] by assuming that the formation of the $AgL^+$ species occurs, with a change of coordination from the initial 4-coordinated solvate to a linear complex. So, the second mononuclear species, $AgL_2^+$, is formed with the replacement of only one solvent molecule by the monodentate ligand. This explanation agrees with the trend of the values of stepwise enthalpies ($-\Delta H°_{K12} > -\Delta H°_{K11}$) and entropies ($-\Delta S°_{K12} > -\Delta S°_{K11}$) and can be extended to the DMSO and DMF solvents where the same phenomenon occurs.

For all the polydentate amines there is no significant entropy changes on going from the first to the second complex formation, as well evident in Fig. 3, where only the thermodynamic functions relative to the second complexation step are reported. Evidently, the entropy lost on the association of the reagents AgL and L to form $AgL_2$ complex is compensated by the disorder gained through desolvation effects, which result more important in this second step, in absence of a previous change of coordination of Ag(I) solvate when complexed by polyamines in 1:1 species. Also, a contribution from the opening of the ligands arms may be considered when DIEN or TRIEN are concerned (see below).


**DMF**

EN and DIEN complexation results in higher stabilities and more favourable $-\Delta H°_{11}$ with respect to *n*-but (with EN intermediate between *n*-but and DIEN, Table 1) which indicates that they behave as bi-and tri-dentate respectively in the first complexation step. This has been evidenced previously also in the case of Co(II) and Cd(II) ions in DMSO by FT-IR spectroscopy[10,13,58,61]. For EN the same seems to be true also in the second complexation step, with the main desolvation occurring in $AgEN_2$ formation (Table 1 and Fig.3). The values of thermodynamic parameters for $AgDIEN_2$

complex formation in DMF were previously discussed[43] and indicated that, for the second complexation step, the high $K_{11}/K_{12}$ ratio (=$10^7$) and the $\Delta H^\circ_{K12}$ and $T\Delta S^\circ_{K12}$ parameters well agreed with the formation of two five-membered chelate rings, in which the ligands acted as bidentate.

A detailed analysis of data for TRIEN in DMF seems to indicate that, despite the $\log\beta_{11}$ is two orders of magnitude higher than for tridentate DIEN, TRIEN does not behave as tetradentate in the first step, as suggested previously in DMSO[32]. The $\Delta H^\circ_{11}$ for TRIEN (-96.5 kJ mol$^{-1}$) is in fact similar to the $\Delta H^\circ_{11}$ for DIEN (-90.4 kJ mol$^{-1}$) and $T\Delta S_{11}^\circ$ is much less unfavourable for TRIEN than for DIEN system. As a matter of fact, the higher stabilization of 1:1 Ag-TRIEN complex with respect to 1:1 Ag-DIEN in DMF is mainly due to the less unfavourable entropy term and therefore to a more disordered system than in AgDIEN, where all the N atoms are supposed to be coordinated to the metal ion.

The fact that TRIEN is not tetradentate in AgTRIEN complex is also supported by the thermodynamic values for the formation of the dinuclear $Ag_2L$ species, according to the reaction:

$$AgL + Ag \rightleftharpoons Ag_2L$$
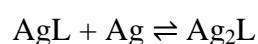
for which $\log K_{21}$=3.11, $\Delta H^\circ_{K21}$ = -33.5 kJmol$^{-1}$, $T\Delta S^\circ_{K21}$ = -21.5 kJmol$^{-1}$. The high favourable $\Delta H^\circ_{21}$ value, very close to to that relative to $n$-but complex formation, $\Delta H^\circ_{11n-but}$ = -36.3 kJmol$^{-1}$, confirms the presence of available amino group in the starting AgTRIEN complex, ready for coordination with an additional Ag(I) ion.

It should be noted that in DMF the formation of polynuclear species is expected to be less favoured than in DMSO where, on the contrary, the $Ag_2L$ species was not detected[32]. Due to the lower dielectric constant (Table 2) the screening of the repulsive cation-cation interaction in polynuclear complexes should be lower in DMF. However, a higher stability of the complexes formed in DMF with respect to DMSO was already observed for $Ag_2L$ complex with the tripodal polypyridinic ligand 6,6'-bis-[bis-(2-pyridylmethyl)aminomethyl]-2,2'-bipyridine (BTPA) and was tentatively explained with the lower Dn of DMF [62] and the fact that the coordination sites should also be at a distance for which repulsion between the two positive charges is not too strong.

*PC.*

In PC, the Ag(I) ion forms complexes of stability higher than those found in DMSO and DMF. This can be easily explained by the transfer parameters for Ag(I) discussed above (Tab. 2) and the relatively weak solvation of amine in PC. On the basis of thermodynamic data, it can be reasonably supposed that both EN and DIEN behave as bi- and-tridentate in the first complexation step. To support this hypothesis and in absence of a direct possible comparison with a monodentate amine, a comparison with data for the complexation with triphenylphosphine (PPh$_3$) in PC can be done[26].

A much lower stability with PPh$_3$ ($\log\beta_{11}$ = 9.95) and especially a much lower enthalpy gain (-70.5 kJ mol$^{-1}$) than that found here for Ag(I)-EN complex formation ($\log\beta_{11}$ = 12.24, $\Delta H°_{11}$ = -95.4 kJ mol$^{-1}$) was reported[26]: this allows to estimate that two Ag(I)-N bonds are formed in the 1:1 Ag-EN complex. In fact, if only one nitrogen atom of EN would be coordinated, a less favourable value of $\Delta H°_{11}$ should be expected for AgEN than for AgPPh$_3$ formation.

A specific feature of speciation in PC is the formation of two different polynuclear species, Ag$_2$DIEN and Ag$_3$DIEN$_2$ in line with what expected on the basis of dielectric properties[44] and with available literature in PC [52].

The formation of Ag$_3$L$_2$ can be seen as derived from the following reaction:

$$Ag_2L + AgL \rightleftharpoons Ag_3L_2$$

for which $\log K_{32}$ = 3.85, $\Delta H°_{K32}$ = -18 and $T\Delta S°_{K32}$ = + 4.4 kJ mol$^{-1}$.

The slightly favorable entropy term indicates that a somewhat lower solvation of the final species with respect to the reagents prevails on the entropy loss associated to Ag$_2$L and AgL aggregation.

## 5. Conclusions.

The stability order for the AgL and AgL$_2$ (L=n-but or polyamines) complexes are strongly influenced by the different solvents and increases in the order: water < DMSO < AN < DMF < PC, reflecting the following order of affinity of silver(I) for the different solvents: DMSO > AN > DMF > water > PC, a part for water. The discrepancy observed for water can be explained as due to a strong solvation, via hydrogen bonds, of primary and secondary polyamines in this solvent.

Additional polynuclear species are highlighted by potentiometric and calorimetric techniques, i.e. Ag$_2$TRIEN species formed in DMF and Ag$_2$DIEN and Ag$_3$DIEN$_2$ species in PC. In particular, the formation of the dinuclear complex in DMF and not in DMSO, is somewhat unexpected, given the

lower $\varepsilon$ value for the former solvent: Ag$_2$TRIEN formation is evidently more influenced by the lower solvation of Ag(I) ion in DMF than by the different $\varepsilon$ values of the two solvents.

**Table 1**. Overall stability constants and thermodynamic functions (kJmol$^{-1}$) of silver(I)-amine complexes in DMF and PC at 298 K and $I = 0.1$ mol dm$^{-3}$; estimated three standard deviations in parentheses. Available data at 298 K in water, DMSO and AN are also inserted.

| | Solvent | Species | $\log\beta_{ij}$ | $-\Delta G_{ij}°$ | $-\Delta H_{ij}°$ | $-T\Delta S_{ij}°$ |
|---|---|---|---|---|---|---|
| Ag-EN | PC | ML | 12.24(4) | 69.9(2) | 95.4(8) | 25.5 |
| | | ML$_2$ | 17.13(6) | 97.8(3) | 124(2) | 26.2 |
| Ag-DIEN | PC | ML | 14.65(4) | 83.6(2) | 108(1) | 24.4 |
| | | ML$_2$ | 17.96(6) | 102.5(3) | 127.6(9) | 25.1 |
| | | M$_2$L | 17.9(3) | 102(2) | 137(3) | 35 |
| | | M$_3$L$_2$ | 36.4(2) | 208(2) | 263(4) | 55 |
| Ag-*n*-but | DMF | ML | 4.80(9)[a] | 27.4(3) | 36.3(9)[a] | 8.9 |
| | | ML$_2$ | 9.59(3) | 54.7(2) | 86.5(5) | 31.8 |
| Ag-EN | DMF | ML | 7.95(4) | 45.4(2) | 76.0(5) | 30.6 |
| | | ML$_2$ | 12.19(3) | 69.6(3) | 105.6(3) | 36 |
| Ag-DIEN[a] | DMF | ML | 10.21(3) | 58.3(1) | 90.4(6) | 32.1 |
| | | ML$_2$ | 13.18(9) | 75.2(5) | 108.8(6) | 33.6 |
| Ag-TRIEN | DMF | ML | 12.96(1) | 74.0(1) | 96.5(6) | 22.5 |
| | | M$_2$L | 15.07(9) | 86.0(5) | 130(9) | 44 |
| Ag-*n*-but[b] | DMSO | ML | 3.58 | 20.46 | 31.4 | 10.94 |
| | | ML$_2$ | 7.42 | 41.86 | 71.5 | 29.64 |
| Ag-EN[c] | DMSO | ML | 5.34 | 30.5 | 63 | 32.5 |
| | | ML$_2$ | 9.5 | 54.2 | 85 | 30.8 |
| Ag-DIEN[c] | DMSO | ML | 7.46 | 42.6 | 78.2 | 35.6 |
| | | ML$_2$ | 10.2 | 58.2 | 94 | 35.8 |
| Ag-TRIEN[d] | DMSO | ML | 10.32 | 58.91 | 91.5 | 32.59 |
| Ag-*n*-but | Water[e] | ML | 3.43 | 19.6 | 16.7 | -2.9 |
| | | ML$_2$ | 7.97 | 45.5 | 52.7 | 7.2 |
| Ag-EN | Water | ML$_2$ | 7.7 | 44.0 | 54.8 | 10.8 |
| Ag-DIEN | Water | ML | 6.1 | | | |
| | | M$_2$L | 7.5 | | | |
| Ag-TRIEN | Water | ML | 7.5 | | | |
| Ag-*n*-but[f] | AN | ML | 3.65 | | | |
| | | ML$_2$ | 7.04 | | | |
| | | ML$_3$ | 7.53 | | | |

a) $\log\beta_{ij}$ and $\Delta H_{ij}$ values from ref. [43]; b) ref. [29]; c) ref. [31]; d) ref. [32]; e) data in water from ref. [1]; f) ref. [40].

**Table 2.** Free energies and enthalpies of transfer, $\Delta G°_{tr}(AN{\rightarrow}solv)$, $\Delta H°_{tr}(AN{\rightarrow}solv)$, for the Ag(I), ion, expressed in kJ mol$^{-1}$, with AN taken as reference solvent [56]. The dielectric constant ($\varepsilon$), donor (Dn) and acceptor (An) numbers are taken from ref. [44].

|  | $\varepsilon$ | An | Dn | $\Delta G°_{tr}$ | $\Delta H°_{tr}$ |
|---|---|---|---|---|---|
| Water | 78.36 | 54.8 | 18 | 22.3 | 41 |
| DMSO | 46.45 | 19.3 | 29.8 | -11.9 | -10 |
| DMF | 36.71 | 16.0 | 26.6 | 7.4 | 6.0 |
| PC | 64.92 | 18.3 | 15.1 | 45.8 | 51.6 |
| AN | 37.50 | 18.9 | 14.1 | --- | --- |
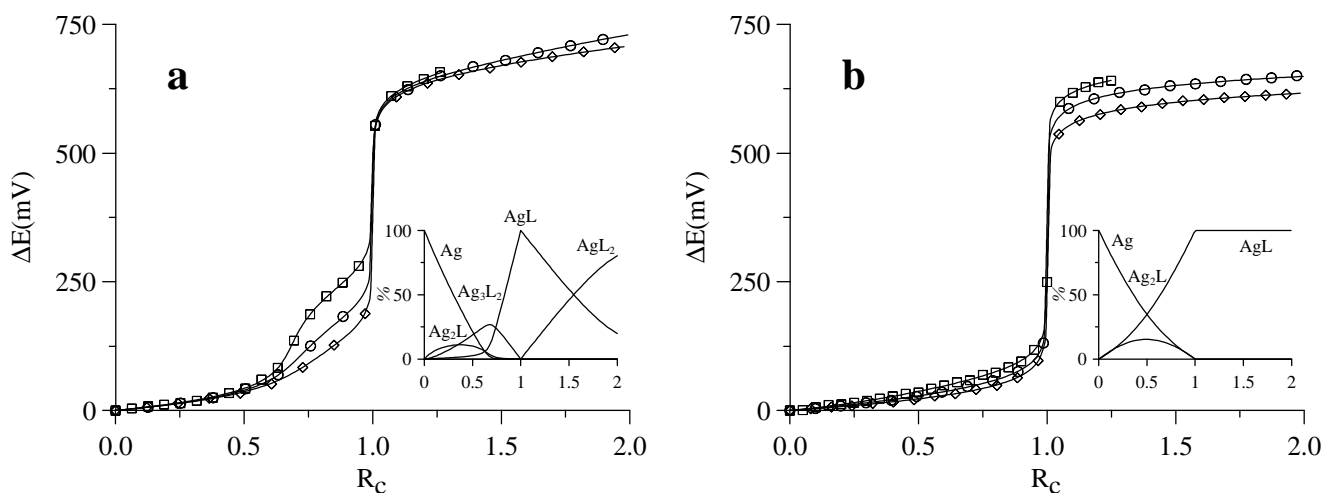


**Figure 1**. Plot of the observed and calculated e.m.f. values for titrations of Ag(I) solutions with: a) DIEN in PC ($\Diamond$) 2.10, (O) 5.02 , ($\Box$) 19.98 mmoldm$^{-3}$ in C$°_{Ag+}$; b) TRIEN in DMF ($\Diamond$) 2.91, (O) 10.33 , ($\Box$) 30.55 mmoldm$^{-3}$ in C$°_{Ag+}$. Insets: speciation plots for a C$°_{Ag+}$ = 10 mmol dm$^{-3}$.
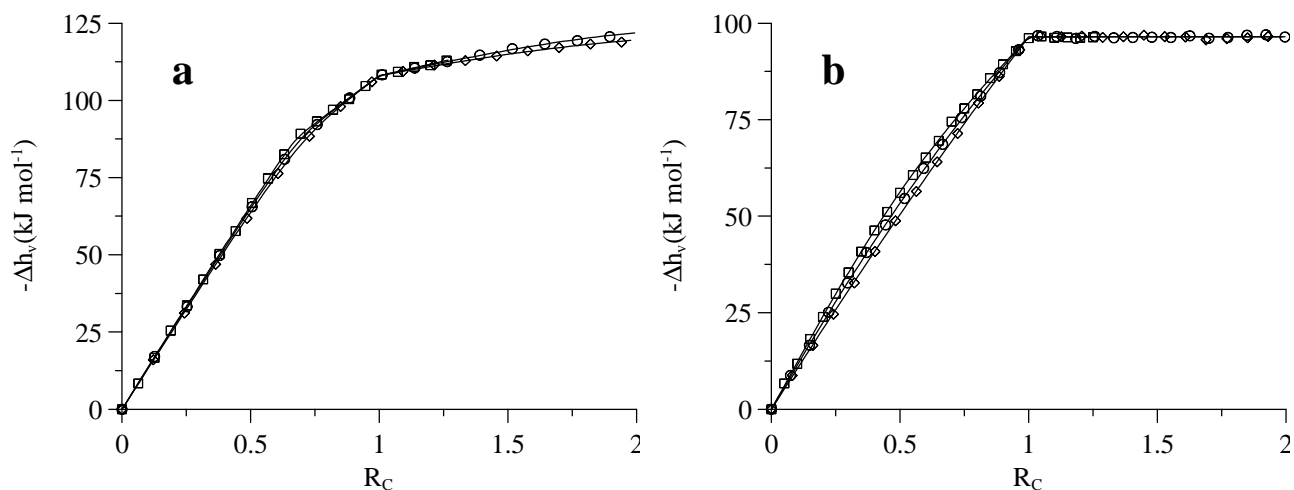
**Figure 2.** The total molar enthalpy changes, $\Delta h_v$, as a function of $R_c = C_L/C_M$ for silver(I) with a) DIEN in PC ($\Diamond$) 2.10, ($\bigcirc$) 5.02, ($\square$) 19.98 mmoldm$^{-3}$ in $C^{\circ}_{Ag+}$; b) TRIEN in DMF ($\Diamond$) 2.91, ($\bigcirc$) 10.33 ($\square$) 30.55 mmoldm$^{-3}$ in $C^{\circ}_{Ag+}$. Only some of the experimental points, chosen at random, have been plotted. The solid lines have been calculated from the values of $\beta_{ij}$ and $\Delta H^{\circ}_{ij}$ in Table 1.

**Figure. 3**. Stepwise thermodynamic functions, **-ΔG°$_{K12}$, -ΔH°$_{K12}$, −TΔS°$_{K12}$**, for the reaction AgL +

L ⇌ AgL$_2$ (L =$n$-but, EN, DIEN) in DMSO, DMF and PC as calculated from Table 1.
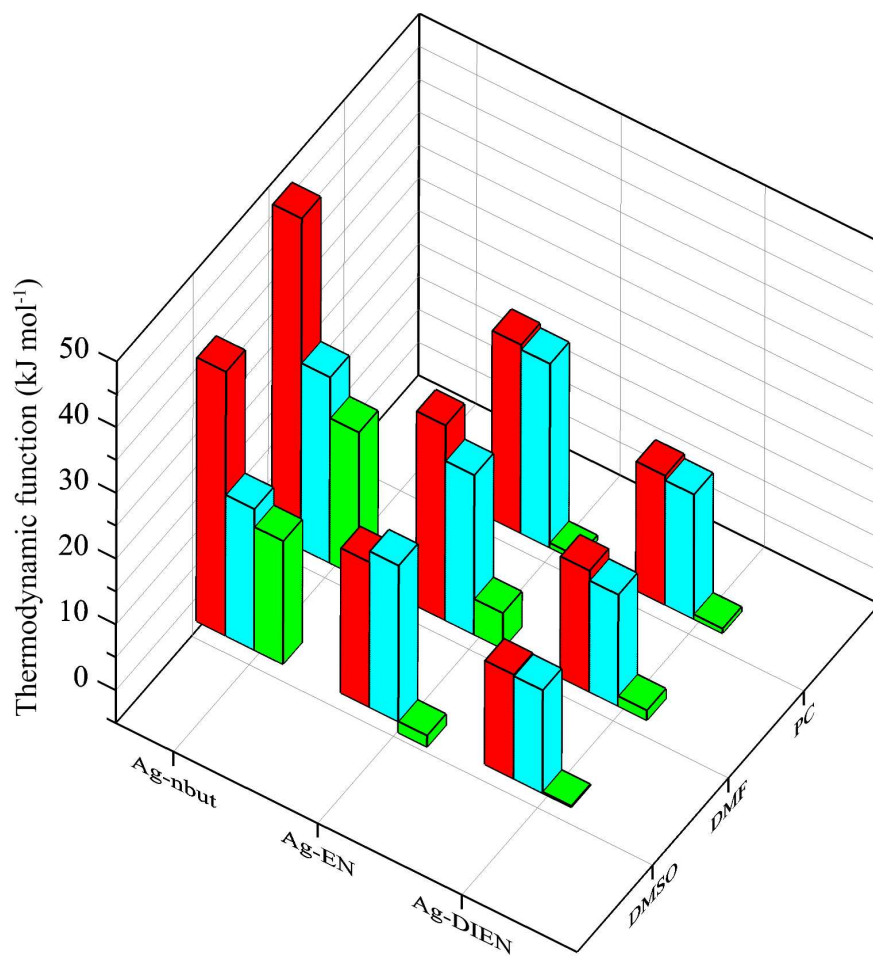
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