

Equilibria between Ag^+ and Aza-Crown Ethers

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Complex-formation equilibria of silver(I) ions and aza-crown ethers and aliphatic amines were studied in acetonitrile, propylene carbonate, and methanol by the potentiometric method. It was found that AgL^+ and AgL_2^+ species (L denoting the organic ligand) are formed. The stability constants of the complexes with crown ethers are greater compared to those with amines. It was found that solvent composition and cavity size of macrocyclic polyethers influence significantly the stability constants of the complexes formed. The difference in stability constants for various crown polyethers is discussed in terms of possible structure of the complexes.

Key words: silver(I), monaza-crown–ether complexes in organic solvents

Silver(I) ions can form the AgL^+ types complexes with aza-crown ethers by either penetration into the cavity of the macrocyclic structure or by forming more complicated sandwich-type and linear AgL_2^+ species; the latter resembling well-known linear complexes with aliphatic amines [1] (Fig. 1). The AgL_2^+ sandwich-like complexes are suggested to form with some aza-crown ethers when the cavity is smaller than the diameter of the silver(I) ion [2].

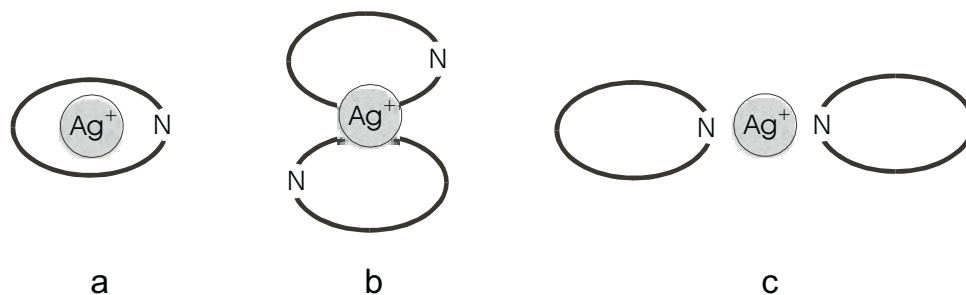


Figure 1. Structures of the aza-crown complexes with the Ag^+ ion. **a.** Internal AgL^+ complex; **b.** Sandwich-like structure of the AgL_2^+ complex; **c.** Linear structure of the AgL_2^+ complex.

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The purpose of this study was to investigate ligand and solvent influences on the stability of AgL^+ and AgL_2^+ complexes and, further to learn, which of the three forms of the complex predominates in the case of a particular ligand and solvent. (We have found in our previous study [3] that some information of the possible structure can be obtained from the differences of the stability constants with different ligands belonging, however, to the same structural family.) We have determined the stability constants of silver(I) ions with the following monoaza-crown ethers: 1,4,7-trioxa-10-azacyclododecane (A12C4), 1,4,7,10-tetraoxa-13-azacyclopentadecane (A15C5), 1,4,7,10,13-pentaoxa-16-azacyclooctadecane (A18C6), 1,4,7,10,13,16-hexaoxa-19-azacyclohenicosane (A21C7) and selected aliphatic amines (treated as reference nitrogen donors): cyclohexylamine, dibutylamine and dipropylamine in propylene carbonate (PC), methanol (MeOH) and acetonitrile (AN) solution (Fig. 2) using the potentiometric method.

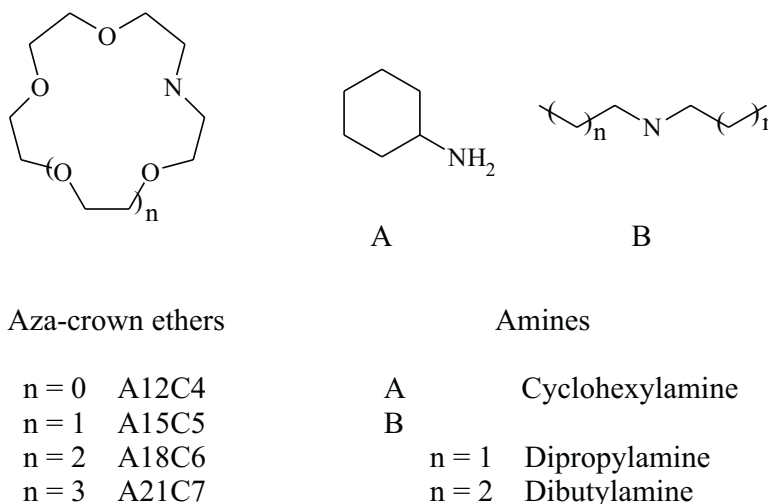


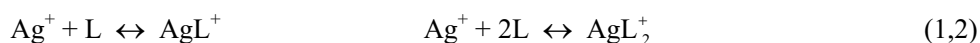
Figure 2. Ligands used in this study.

EXPERIMENTAL

A15C5 (Merck) and A18C6 (Merck) were distilled before use in Kugelrohr apparatus [4]. A12C4 and A21C7 were obtained according to the procedure described earlier [4]. Silver(I) perchlorate (Fluka) and tetraethylammonium perchlorate (TEAP; Fluka) were recrystallized and dried under vacuum [5]. Propylene carbonate (Merck), methanol (Merck), acetonitrile (BDH) were of the highest purity available and were used as purchased without further purification. Cyclohexylamine, dibutylamine, and dipropylamine (Merck) were purified as described in [5]. Potentiometric measurements were carried out using a procedure described in [3]. The measurement cell was a bipartite reaction vessel with the half-cells connected by a salt bridge containing 0.1 mol dm^{-3} TEAP in the same solvent. The reference electrode used in all titrations was an Ag/Ag^+ electrode, which was immersed in the same solvent as that used in investigation. The silver(I) concentration was determined using silver-wire electrode dipped in the solution connected to an OP-205 Radelkis pH-meter, which was interfaced to a computer. The ligand solution (5.0×10^{-3} to $1.2 \times 10^{-2} \text{ mol dm}^{-3}$) was added stepwise with a 0.5 ml Hamilton microsyringe equipped with a gauge 30 tube to 2 ml of silver salt solutions ($5\text{--}8 \times 10^{-4} \text{ mol dm}^{-3}$). The ionic strength of solutions was kept constant at $I = 0.1 \text{ mol dm}^{-3}$ by adding 0.1 M TEAP.

RESULTS AND DISCUSSION

On the potentiometric titration curves a double potential jump was observed only in PC solutions for the A15C5 + Ag^+ system (Fig. 3B). It indicated that ligand A15C5 forms with silver(I) 1:1 and 1:2 type complexes. The equilibria in the solution are described by:



For other investigated systems a single jump was observed (Fig. 3A). The shape of potentiometric titration curves of the aza-crown ethers in AN, MeOH and PC – silver(I) system suggests that apart from the equilibrium resulting in the formation of the AgL^+ ion, the other equilibria are also likely to occur. Attempts of fitting the curves to data points have shown that the variations of the potential as a function of the titrant added are best represented by a set of two equilibria.

The stability constants of the AgL^+ and AgL_2^+ complexes were determined as $\log K_1$, and $\log \beta_2$ ((1) and (2) respectively). The equilibrium constants and the fitting curves were calculated using a STOICHTO [6–7] programme based on the non-linear least-squares Gauss-Newton-Marquardt algorithm [8]. The fitting procedures allow to elucidate both equilibria constants. Model 2 (AgL^+ and AgL_2^+) fits the curves to the experimental data points significantly better than the model (1) (AgL^+) as revealed by a significant decrease of the residual variance δ^2 and the standard deviation in the e.m.f. σ_E (Table 1). Including more species (Ag_2L^+ , $\text{Ag}_2\text{L}_3^{2+}$, $\text{Ag}_3\text{L}_2^{3+}$) in addition to AgL^+ and AgL_2^+ was statistically insignificant, as judged on the basis of the F-test (of the significance level 95%). It can therefore be concluded that the model containing AgL^+ and AgL_2^+ is significant to describe the equilibrium systems under study. Adopting model 2 to A21C7 gives relatively inferior fit than to the other aza-crown ethers. This can be explained in terms of setting up equilibria, leading to other species, for instance $\text{Ag}_2\text{L}_3^{2+}$ and $\text{Ag}_3\text{L}_2^{3+}$ as it was shown in our previous work [3]. Selected titration curves in PC and the corresponding fitting curves are presented in Fig. 3. The $\log K_1$ and $\log \beta_2$ values calculated on the basis of potentiometric titrations in the three solvents are given in Table 2.

Similar equilibria involving crown ethers containing chromophore as a pendant arms have been reported for alkali metal ions [9–10] and the Ag^+ ion [3,11]. Agreement of the presented data with literature is good, except $\log \beta_2$ of Ag^+ with monoaza-crown ether in AN [12]. This can be caused by the different procedure used for estimation of $\log \beta_2$.

The primary and secondary investigated amines form with silver(I) ion 1:1 (AgL^+) and 1:2 (AgL_2^+) complexes in PC, MeOH and AN solutions. The data obtained, according to Model 2, using above fitting procedure, are presented in Table 3. In all solutions investigated the stability constants are larger for primary amines than for secondary ones and in the experimental conditions are practically independent of the lengths of amine alkyl groups.

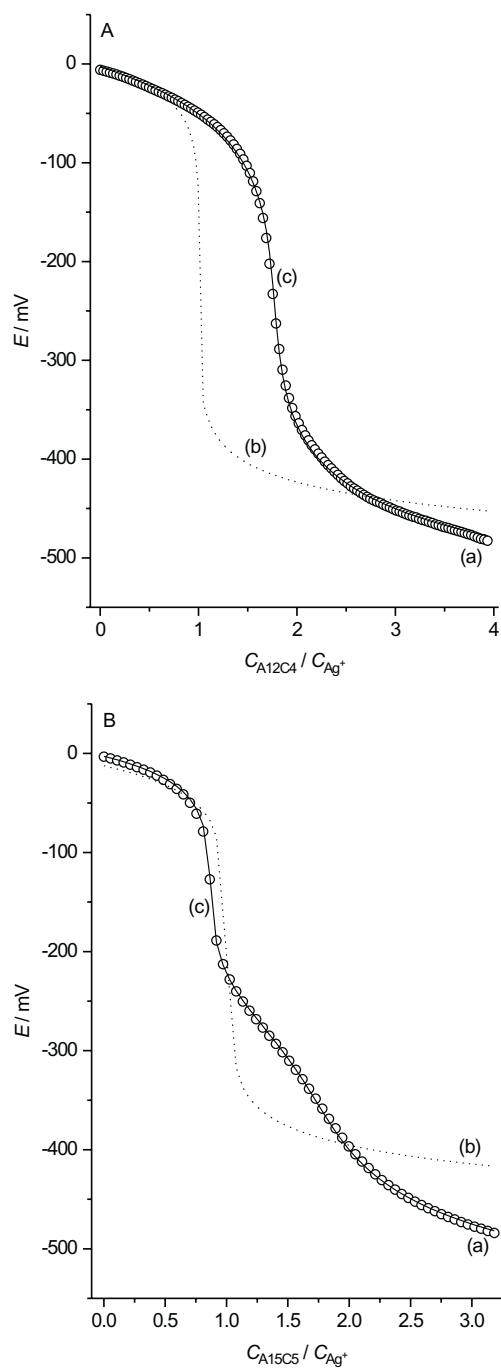


Figure 3. Results of potentiometric titrations of $AgClO_4$ (6.00×10^{-4} M) in propylene carbonate with aza-crown ethers ($0-2.00 \times 10^{-3}$ M) vs. molar ratio $C_{\text{monoaza-crown ether}}/C_{Ag^+}$. Data points (a, open circles) and fitting curves for model 1 (b, dotted line) and 2 (c, solid line). A, B, denote respectively A12C4 and A15C5.

Table 1. Results of fitting of equilibrium models to potentiometric data.

Ligand	Model	Species considered	σ^2 ^a	σ_E ^b
A12C4	1	AgL^+	223.3	22
	2	$\text{AgL}^+, \text{AgL}_2^+$	8.8	3
A15C5	1	AgL^+	611.7	48
	2	$\text{AgL}^+, \text{AgL}_2^+$	3.4	2
A18C6	1	AgL^+	41.1	12
	2	$\text{AgL}^+, \text{AgL}_2^+$	9.5	6
A21C7	1	AgL^+	207.5	26
	2	$\text{AgL}^+, \text{AgL}_2^+$	50.7	6

^a Residual variance: $\sigma^2 = \omega(x)/(n-p)$, p is the number of parameters, n is the number of experimental points, $\omega(x)$ is the sum of the squares of the differences between measured and calculated values (e.m.f. and titrant volumes). ^b σ_E = standard deviation in e.m.f.; $\sigma = (\sigma^2)^{1/2}$.

Table 2. Stability constants of the silver(I) complexes of macrocyclic ligands in propylene carbonate (PC), methanol (MeOH) and acetonitrile (AN) at 25°C.

Aza-crown ether	PC		MeOH		AN	
	$\log K_1$	$\log \beta_2$	$\log K_1$	$\log \beta_2$	$\log K_1$	$\log \beta_2$
A12C4	8.73 ± 0.07	14.21 ± 0.07	3.93 ± 0.06	7.47 ± 0.07	3.50 ± 0.02 3.73^c	6.96 ± 0.04 6.80^c
A15C5	9.75 ± 0.04^a 9.65^b	14.52 ± 0.08^a 14.4^b	5.52 ± 0.05 5.48^b	8.56 ± 0.05 8.33^b	4.40 ± 0.06 4.10^c	7.23 ± 0.09 6.55^c
A18C6	10.17 ± 0.03 10.31^b	13.54 ± 0.05 13.34^b	6.01 ± 0.03 6.03^b	8.85 ± 0.04 8.38^b	3.42 ± 0.02 3.56^c	6.08 ± 0.04 5.40^c
A21C7	9.53 ± 0.04	13.41 ± 0.04	5.17 ± 0.04	8.21 ± 0.06	3.08 ± 0.03	5.97 ± 0.04

^a Ref. [3]; ^b Ref. [11]; ^c Ref. [12].

Table 3. Stability constants of the silver(I) complexes with amines in propylene carbonate (PC), methanol (MeOH) and acetonitrile (AN) at 25°C.

Amine	PC		MeOH		AN	
	$\log K_1$	$\log \beta_2$	$\log K_1$	$\log \beta_2$	$\log K_1$	$\log \beta_2$
Cyclohexylamine	7.23 ± 0.08	14.44 ± 0.09	3.94 ± 0.06	7.89 ± 0.06	3.72 ± 0.04	7.31 ± 0.04
Dibutylamine	6.46 ± 0.07	12.85 ± 0.07	3.42 ± 0.06	6.89 ± 0.06	3.02 ± 0.05 3.26^a	6.17 ± 0.04 5.94^a
Dipropylamine	6.36 ± 0.08	12.62 ± 0.07	3.36 ± 0.05	6.78 ± 0.09	2.94 ± 0.06	6.02 ± 0.08

^a Ref. [12].

Complex formation between silver(I) and amines [13], aza-crown ether and cryptand in polar solvents was studied earlier [11,14]. Primary and secondary aliphatic mono-amines in aqueous and polar organic solvents form AgL^+ complexes with silver(I). The maximum coordination number of Ag^+ in dilute solutions of the monoaza-crown ethers is equal to two [1]. The literature data show that the silver(I)

cation complexed by cryptates is well shielded from solvent [14]. Silver(I) forms only 1:1 inclusion complexes with cryptand and diaza-crown ethers. The silver(I) cation complexed by cryptates is well shielded from interaction with the solvent [11,19]. In all other complexes the cations interact with solvent molecules [19].

The stepwise stability constants of AgL^+ and AgL_2^+ are similar (Table 2). The K_1 and cumulative stability constants depend on solvent and decrease in the order $\text{PC} > \text{MeOH} > \text{AN}$. In the case of aliphatic amines the stability constants (K_1) of their complexes with Ag^+ ion are distinctly lower than those of the monoaza-crown ethers. This can be explained in terms of the obvious absence of additional stabilization energy of the Ag^+ ion because of the macrocyclic effect [15].

The comparison of the stability constants for the successive binding of two ligand molecules (K_1/K_2) is presented in Table 4. For all amines and all solvents the ratio of K_1/K_2 was lower than four (as opposed to crown ethers), the value characteristic for purely statistical linearly coordinated [12,16]. This means that the attachment of the first ligand molecules enhances the binding of the second one. This can be caused by the differences in the geometries of solvation and coordination at the silver(I) ion and also by changes in electron density, connected with hybridization and back coordination effect [1].

Table 4. Values of K_1/K_2 for the silver(I) complexes with monoaza-crown ethers and amines in different organic solvents.

Ligands	K_1/K_2		
	PC	MeOH	AN
A12C4	1.78×10^3	2.45	1.1 4.6 ^a
A15C5	9.55×10^4	3.01×10^2	37.1 45 ^a
A18C6	6.36×10^6	1.48×10^3	5.75 52 ^a
A21C7	4.47×10^5	1.35×10^2	1.54
Cyclohexylamine	1.05	0.98	1.35
Dibutylamine	1.17	0.89	0.74 3.8 ^a
Dipropylamine	1.26	0.87	0.72

^a Ref. [12].

In the series of the aza-crown ethers studied, the stability constants of the AgL^+ complexes depend on the ring size of the ligand. The greatest stability constants were obtained for A15C5 in AN solutions and for A18C6 in PC and MeOH solutions. The crystallographic radius of Ag^+ ($r = 1.26 \text{ \AA}$ [17]) is very similar to the cavity radii of the A15C5 ($r = 0.85\text{--}1.1 \text{ \AA}$ [17]) and A18C6 ($r = 1.3\text{--}1.6 \text{ \AA}$ [17]) ligands. This suggests that silver cations should fit well to the ring cavity of both monoaza-crown ethers.

The ring size of A21C7 ($r = 1.65\text{--}2.15 \text{ \AA}$ [17]) and A12C4 ($r = 0.6\text{--}0.75 \text{ \AA}$ [17]) monoaza-crown ethers are too large or too small, respectively, for the silver(I) ion to fit, what results in the reduction of stability constant K_1 . This suggests that the monoaza-crown ethers should form inclusion-type AgL^+ complexes with silver(I) in all investigated solvents. This conclusion is supported by higher values of the K_1/K_2 ratio (Table 4), as opposed to those of the amines considered in this study. The values of K_1/K_2 depend strongly on solvent properties. For all silver(I) complexes with monoaza-crown ethers the K_1/K_2 values are higher than four in PC, which has weak solvating properties with respect to Ag^+ [18]. Only for A12C4 in MeOH and for A12C4 and A21C7 in AN the K_1/K_2 values are lower than 4, which suggests that the 1:1 inclusion complexes cannot be formed in those cases.

The comparison of the stability constants of silver(I) with the ligands in the solvents considered in this study shows that the values of K_1 of Ag^+ – monoaza-crown ethers complexes are higher (Table 2) than those of Ag^+ – aliphatic amines complexes (Table 3), but the K_2 stability constants are lower. This can be explained in terms of active participation of the ether oxygen atoms in the formation of AgL^+ inclusion complexes. The same interactions can also occur in the case of silver(I) complexes with A12C4 and A21C7 in PC and MeOH solutions, because these ligands have too small or too large cavity to form stable inclusion complexes.

The data presented in Tables 2–3 show that the solvent also has a pronounced effect on complexation equilibria. The relationship between $\log \beta_2$ values in two different solvents (PC and AN) is linear for the crown ethers with the slope of 1.18 and correlation coefficient $R = 0.997$ (Fig. 4). A similar relationship is obtained for the aliphatic amines, the slope and the correlation coefficient being 0.71 and 0.999 respectively (Figure 4). For Ag^+ complexes with aliphatic amines in MeOH and PC the slope and the correlation coefficient being 0.62 and 0.999 respectively, but for monoaza-crown ethers the $\log \beta_2$ values in MeOH are uncorrelated with those in PC (Fig. 4). This suggests that the MeOH molecules strongly interact with monoaza-crown ethers ligands, probably by protonating or forming strong hydrogen bonds with amine nitrogen, as observed in other studies [19,20].

Application of the Born-Haber cycle to the complex formation reactions (4) and (5) in two solvents leads to the following relationships between stability constants and free energies of transfer of the species involved in the equilibrium [14,21]:

$$-2.303RT \log \frac{K_1(S)}{K_1(PC)} = \Delta G_{tr}(AgL^+) - \Delta G_{tr}(L) - \Delta G_{tr}(Ag^+) \quad (4)$$

$$-2.303RT \log \frac{\beta_2(S)}{\beta_2(PC)} = \Delta G_{tr}(AgL_2^+) - 2\Delta G_{tr}(L) - \Delta G_{tr}(Ag^+) \quad (5)$$

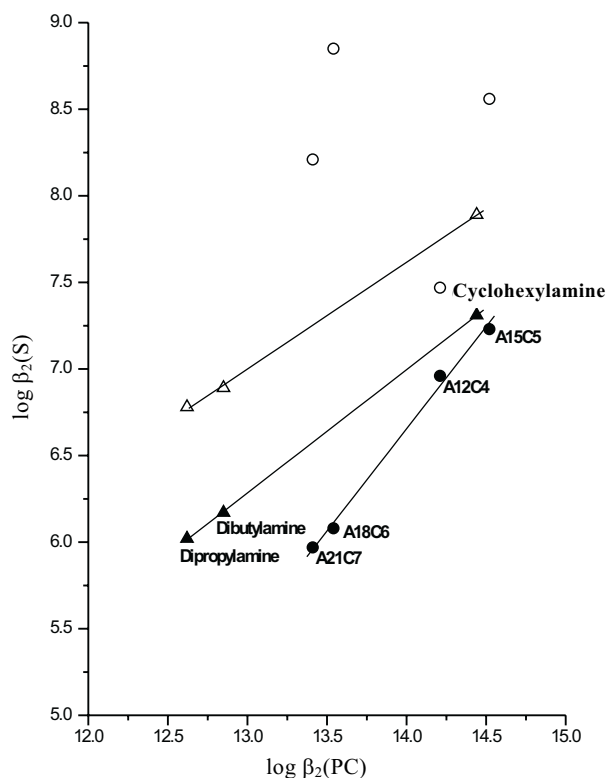


Figure 4. Stability constants ($\log \beta_2$) of the aza-crown and aliphatic amine complexes of Ag^+ in propylene carbonate (PC) vs. $\log \beta_2$ in acetonitrile (AN) ●, ▲ or MeOH ○, △ at 25°C. For monoaza-crown ethers complexes ●, ○ and for aliphatic amines complexes △, ▲.

Substitution of the free energy of transfer of Ag^+ into (4) and (5) gives the difference of the free energy of transfer of complexes and the corresponding ligands, the values obtained are presented in Table 5.

Table 5. Differences in the free energies of transfer from propylene carbonate (PC) to methanol (MeOH) and acetonitrile (AN) between Ag^+ complexes and ligand at 25°C.

Ligand	$\Delta G_{\text{tr}}(\text{AgL}^+) - \Delta G_{\text{tr}}(\text{L})$ [kJ/mol]		$\Delta G_{\text{tr}}(\text{AgL}_2^+) - 2\Delta G_{\text{tr}}(\text{L})$ [kJ/mol]	
	AN	MeOH	AN	MeOH
A12C4	-12.1	15.4	-0.6	26.3
A15C5	-11.5	11.9	-0.4	21.8
A18C6	-3.5	11.6	0.6	14.6
A21C7	-5.2	12.7	0.5	28.5
Cyclohexylamine	-22.0	6.5	-1.3	25.2
Dibutylamine	-22.4	5.2	-3.9	21.8
Dipropylamine	-22.5	4.9	-4.3	21.3

The free energy of transfer, ΔG_{tr} , of silver(I) from PC to other organic solvents changes in the order DMSO (-53.6 kJ/mol) < AN (-42.0 kJ/mol) < MeOH (-12.2 kJ/mol) [18]. There is some evidence that the Ag^+ ions are more strongly solvated in DMSO, AN and MeOH than in PC solutions, what conforms with the obtained negative ΔG_{tr} values.

For the silver(I) complexes with monoaza-crown ethers the differences of $\Delta G_{\text{tr}}(\text{AgL}^+) - \Delta G_{\text{tr}}(\text{L})$ in AN and DMSO [12] solutions are less negative than for silver(I) complexes with the aliphatic amines investigated. This means that the silver(I) ions are not completely shielded from interaction with solvent molecules in the AgL^+ complexes. Conversely, silver(I) ions are well shielded from interactions with AN molecules in AgL_2^+ monoaza-crown ethers complexes, because the $\Delta G_{\text{tr}}(\text{Ag}_2\text{L}^+) - 2\Delta G_{\text{tr}}(\text{L})$ values are close to zero. This suggests that the AgL_2^+ complexes with monoaza-crown ethers ligands have a sandwich-like structure.

The MeOH solutions are more complex. In this case $\Delta G_{\text{tr}}(\text{AgL}^+) - \Delta G_{\text{tr}}(\text{L})$ and $\Delta G_{\text{tr}}(\text{Ag}_2\text{L}^+) - 2\Delta G_{\text{tr}}(\text{L})$ are positive for all ligands investigated. This substantial difference can be connected with ligand protonation or hydrogen-bonding by MeOH molecules and this is a reason of the decrease of the stability constants of AgL^+ and AgL_2^+ complexes. The stability constants in MeOH are usually similar to those observed in AN (Tables 2, 3) and DMSO [12,22], which strongly solvate the silver(I) ions.

Acknowledgments

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