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Stability constants of aza-oxa-crown ether complexes with silver(I) in nonaqueous polar solvents

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Abstract

Complex formation between the silver(I) ion and monoaza- and diaza-crown ethers has been studied in five polar, nonaqueous solvents using potentiometric techniques. The stability constants are spread over seven orders of magnitude, and the major contributor to this variation is the solvation of the silver(I) cation. The ring-size dependence of the stability constants is determined both by the correspondence of the diameters of the silver(I) ion and the ring-cavity size of the macrocycles, and by specific ligand effects including association complex formation between the ligands and the solvent molecules and conformational effects in the free ligands. In the 1:1 complexes of the silver(I) ion with monoaza- and diaza-crown ethers the dominant interaction is between the silver(I) ion and the ligand's nitrogen atoms, but the ether–oxygen atoms also interact with the silver(I) ion. In the AgL_2^+ complexes (L = monoaza-crown ether), however, the monoaza-crown ethers coordinate as monodentate ligands, as with simple mono-amine complexants. In these complexes the ethoxy-chains prevent direct interaction between the silver(I) cation and the solvent molecules, with the result that in dipolar aprotic solvents the free energies of transfer of the ligands and the complexes are equivalent, i.e. the so-called cryptate hypothesis holds for the AgL_2^+ complexes.

Keywords: Polar solvents; Aza-oxa-crown ether complexes; Ligand; Silver(I) ion

1. Introduction

The coordination and solvation of the silver(I) ion depend more strongly upon specific properties of donor atoms of the ligand and solvent molecules, respectively, than on their dipole moments and dielectric constants [1]. A consequence of this is that silver(I), along with copper(I) and gold(I), exhibits unusual behaviour amongst univalent cations, particularly when compared with the alkali metal cations. The solvation structure of the silver(I) cation in the case of salts such as silver perchlorate [2], which have inert anions, in protic and polar aprotic solvents corresponds to a four-coordinate, tetrahedral arrangement of solvent molecules [3]. $AgClO_4$ also forms stable, four-coordinate, tetrahedral solvates with acetonitrile [4] and dimethylsulfoxide [5,6]. The addition of aliphatic mono-amines to solutions of Ag^+ in polar solvents [7,8], however, even for strongly coordinating acetonitrile [9] and dimethylsulfoxide [9,10], results in the formation of quantitatively analysable Ag^+-amine complexes, which have a maximum coordination number of two. In these complexes the arrangement of the silver(I) cation and the two amines is linear, and this may be explained quantum-chemically in terms of hybridisations of the $4d_{z^2}$-, 5s- and $5p_z$-orbitals of the silver(I) ion [11].

The preference shown by Ag^+ for aliphatic amines over polar solvent molecules—with the exception of thio-compounds, such as dimethylthio-formamide [12]—is more suprising when one compares the dielectric constants (ε_r) and dipole moments (μ) of solvating and coordinating molecules. Polar aprotic and protic solvents [13] are typically differentiated from apolar, aprotic solvents [14] in solvent classifications through having dielectric constants in excess of somewhat arbitrarily chosen values of $\varepsilon_r = 15$ [13] or 30 [15] and dipole moments greater than $\mu = 2.5$ D [14].

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Amongst the aliphatic amines, the tertiary compounds are typical apolar aprotic solvents, with dielectric constants $\varepsilon_r < 5$ and dipole moments $\mu < 1.40$ [16]. The related primary and secondary amines, although not able to be assigned clearly to either the polar or apolar class because of their hydrogen bonding abilities [14], have dielectric constants and dipole moments which are not larger than those of the tertiary amines [16]. On purely electrostatic grounds, therefore, they would be expected to interact weakly with Ag^+. The ability of aliphatic monodentate amine ligands to displace solvating molecules such as acetonitrile from the coordination sphere of Ag^+, even in dilute solutions of the amines in acetonitrile, where the solvent molecules are in 10^4 fold excess of the amines, therefore, indicates strongly that electrostatic interactions between Ag^+ and amine molecules play an insignificant role in the complexation reactions. The dominant twofold linear geometry of the amine complexes does, however, give way to fourfold tetrahedral coordination as the concentration of amine molecules increases. Tetrahedral geometry has, for example, been observed in Ag^+ solutions in pure *n*-propylamine using the EXAFS [6]. One may perhaps assume that a linear $N–Ag^+–N$ geometry dominates except where the complex is formed in the presence of less strongly interacting solvent molecules in the liquid state [9], or anions in the crystalline state [6].

These relatively simple generalisations do not hold for chelates involving polyaza-ligands. Here the coordination geometry and stability of the silver(I) complexes are determined more by steric restrictions and the sizes of the chelate rings. Additional considerations arise for interactions with macrocyclic ligands. In such ligands, potentially destabilising repulsions between donor groups, which are of considerable importance in neighbouring monodentate ligands or solvent molecules in the coordination sphere of the cation, are built in during the course of the synthesis of the molecules [17]. This results in considerable enhancement of the stability of metal ions when forming inclusion complexes with macrocyclic ligands, and also places prime importance on the relative sizes of the metal cation and the macrocycle's ring cavity.

The present paper reports values of stability constants of silver(I) complexes with several monoaza- and diaza-crown ethers in five polar solvents. Using the data, it is possible to estimate the difference between the free energies of transfer of the crown ethers and their complexes, and these are discussed in relation to influence of ring size and solvation. The investigation is a continuation of earlier work in which the effect of the nature and distribution of donor atoms in the 18-crown-6 rings on the stabilities of silver(I) complexes were studied [18].

2. Experimetal

2.1. Materials

Acetonitrile (AN), dimethylsulfoxide (DMSO), methanol (MeOH), ethanol (EtOH), nitromethane (NM) and propylene carbonate (PC), all of highest purity (Merck), were used as purchased. The methods of preparation and purification of silver perchlorate and tetraethylammonium perchlorate (TEAP) were similar to those described previously [19].

2.2. Ligands

Monoaza-12-crown-4 (A12C4), monoaza-15-crown-5 (A15C5) and monoaza-18-crown-6 (A18C6) were used as supplied from Aldrich. Monoaza-21-crown-7 (A21C7) was prepared by a method similar to that in the literature [20]. 1,7-Diaza-15-crown-5 ($A_2$15C5, (2,1)), 1,10-diaza-18-crown-6 ($A_2$18C6, (2,2)), 1,13-diaza-21-crown-7 ($A_2$21C7, (2,3)) were purchased from Merck and used without purification. The purity ($\geq$ 97%) of the macrocycles was checked using equivalent-point analysis of pAg-titrations.

2.3. Potentiometric titrations

Stability constants K_{11} (Eq. (1)) and β_{12} (Eq. (2)) for the silver(I) complexes AgL^+ and $AgL_2{}^+$ were determined by at least triplicated potentiometric titrations of $AgClO_4$ solutions (5×10^{-4}–1×10^{-3} M) with ligand solutions (5×10^{-3}–1×10^{-2} M). All titrations were carried out in a thermostated (25.0 °C) bipartite titration vessel whose two compartments were of equal size. The compartments were each filled with 1.5 ml of the same $AgClO_4$ solution, connected by a salt bridge, which is limited by glass frits. They were equipped with silver-wire electrodes and used as reaction and reference half-cells, respectively, of a galvanic element with transport. The two silver-wire electrodes were connected to a digital voltmeter of high input-resistence (Keithley 197). In the progress of titration, equal volumes of ligand solution and solvent were added simultaneously and stepwise to the reaction and reference half-cell, respectively, using two titration apparatuses (Metrohm, Multi-Dosimat 645) which proceed in volume steps of 0.02 or 0.05 ml. This procedure ensures that convective exchange of solutions across the glass frits of the salt bridge is minimised, and that the total concentrations of silver ions and the ionic strengths of the solutions in both half-cells are equal at each titration step. The majority of experiments were performed with silver perchlorate and the ligand dissolved in the pure solvent. In a few experiments, however, solutions held at an ionic strength of 0.05 M using TEAP were favoured. The experiments were performed under the control of a personal computer, which stored the electric potentials and subsequently calculated the stability constants for the equilibria. The calculation procedures of the stability constants were similar to those described previously [21].

$$Ag^+ + L \overset{K_{11}}{\leftrightarrow} AgL^+ \quad (1)$$

$$Ag^+ + 2L \overset{\beta_{12}}{\leftrightarrow} AgL_2^+ \quad (2)$$

3. Results

The four monoaza-crown ethers, from A12C4 to A21C7, form only 1:1- and 1:2-complexes with the silver(I) cation in the five polar solvents studied. The stability constants of the 1:1 complexes, Eq. (1), and the overall stability constants (stability products) of AgL_2^+, Eq. (2), are listed in Table 1. The complexes were in all cases sufficiently stable to allow calculation of the stability constants with good accuracy.

Even in DMSO, where the weakest complexes are found, the potential difference attained at the end of the titrations under the experimental conditions of this study ($C_L/C_{Ag} = 26$) was −43 mV. This may be compared with the fluctuations in the diffusion potentials prior to the start of the experiments, which were less than 1 mV.

There was no indication from the concentration dependence of the electric potentials in solutions containing a considerable excess of ligand over silver(I) ion that complexes containing more than two monoaza-crown ether ligands per silver(I) ion were performed in measurable amounts.

Stability constants for the diaza-crown ethers are listed in Table 2. With one exception, exclusive formation of 1:1 complexes of the diaza-crowns with Ag^+ was always observed. In PC alone, at the highest excess of A_215C5 over Ag^+, the stability constant for the formation of the 1:2 complex could be obtained: $\log \beta_{12} = 16.26 \pm 0.15$.

Table 2
Stability constants ($\log(K_{11}/M^{-1})$) of 1:1 silver(I) complexes with diaza-crown ethers at 25 °C

Ligand	A_215C5	A_218C6	A_221C7
MeOH	7.49±0.01 7.45 [c]	9.99 [a]; 10.18 [b] 10.02 [d]	9.42±0.02 9.29 [c]; 9.60 [d]
EtOH	7.37±0.01	9.43±0.02	9.29±0.01
DMSO	5.71±0.02 [e]	7.39 [a]	6.74±0.04 [e]
AN	6.43±0.01 [f] 6.11 [g]; 6.55 [d]	7.94 [a] 7.76 [g]	7.94±0.02 [f]
PC	13.15±0.05 13.30 [h]	15.57 [a] 15.50 [i]	14.92±0.03
NM	10.25±0.05 [j]	13.01±0.08 [j] 13.63 [b], 13.30 [b]	12.72±0.02 [j]

[a] Ref. [23].
[b] Ref. [24].
[c] Ref. [25].
[d] Ref. [26].
[e] Ref. [9].
[f] Ref. [21].
[g] Ref. [27].
[h] Ref. [28].
[i] Ref. [29].
[j] Ref. [22].

4. Discussion

4.1. Solvents and solvation

The five polar solvents used in this investigation (Table 3) can be separated into protic solvents (MeOH, EtOH) and dipolar aprotic solvents (DMSO,

Table 1
Stability constants ($\log(K_{11}/M^{-1})$) of 1:1 silver(I) complexes and cumulative stability constants ($\log(\beta_{12}/M^{-2})$) of 1:2 silver(I) complexes with monoaza-crown ethers at 25 °C

	Ligand L	A12C4	A15C5	A18C6	A21C7
MeOH	$\log K_{11}$	4.34±0.01	5.48±0.06	6.08±0.04	5.27±0.01
MeOH	$\log \beta_{12}$	8.14±0.01	8.33±0.06	8.43±0.08	8.34±0.07
EtOH	$\log K_{11}$	4.35±0.05	5.52±0.04	5.89±0.04	5.17±0.05
EtOH	$\log \beta_{12}$	8.16±0.05	8.45±0.07	8.19±0.07	8.17±0.05
DMSO	$\log K_{11}$	3.24±0.04 [a]	3.30±0.06 [a]	3.05±0.06 [a]	2.96±0.15
DMSO	$\log \beta_{12}$	5.96±0.10 [a]	5.26±0.07 [a]	4.64±0.06 [a]	5.47±0.15
AN	$\log K_{11}$	3.73±0.04 [b]	4.10±0.13 [b]	3.56±0.02 [b]	3.38±0.04
AN	$\log \beta_{12}$	6.80±0.06 [b]	6.55±0.16 [b]	5.40±0.04 [b]	5.86±0.07
PC	$\log K_{11}$	8.62±0.09	9.65±0.04	10.31±0.07	9.81±0.05
PC	$\log \beta_{12}$	14.67±0.10	14.40±0.04	13.34±0.07	13.66±0.05
NM	$\log K_{11}$	–	-	7.85±0.08 [c]	8.44±0.11 [c]
NM	$\log \beta_{12}$	11.92±0.08 [c]	12.05±0.09 [c]	11.53±0.11 [c]	12.32±0.11 [c]

[a] Ref. [21].
[b] Ref. [9].
[c] Ref. [22].

Table 3
Donor numbers (DN) and transfer free energies of Ag^+ and $A_2 18C6$

Solvent, S	DN [a]	$\Delta G^{\circ}_{tr}(Ag^+; PC \rightarrow S)$ [b,c]	$\Delta G^{\circ}_{tr}(A_2 18C6; PC \rightarrow S)$ [c,d]d
MeOH	19.0	−12.2	−3.6
EtOH	20.0	−13.9	−2.2
DMSO	29.8	−53.6	−0.4
AN	14.1	−42.0	−1.0
PC	15.1	0.0	0.0

[a] Ref. [32].
[b] Ref. [30].
[c] kJ mol^{-1}.
[d] Ref. [23].

AN, PC). The latter are arranged in order of decreasing strength of solvating of the silver(I) cation. The relative energies of the ion–solvent interactions are represented here by the free energy of transfer, $\Delta G_{tr}(Ag^+; PC \rightarrow S)$, the difference between the free energy of solvation of the cation in solvent S and in PC, which has been chosen as the reference solvent [30]. Propylene carbonate is a convenient choice as reference solvent because of its high dielectric constant [15], its lack of specific interactions with cations, and its frequent use as a reference solvent in the literature [31]. A further indicator of the strength of ion–solvent interactions, useful particularly for closed-shell cations [32], the donor numbers, DN, for the solvents are also included in Table 3. These show very clearly the peculiarity of the silver(I) cation in comparison with other monovalent metal cations. Thus the donor numbers would suggest a high degree of similarity between AN and PC in their interactions with the silver(I) ion in sharp contrast to the observed free energies of transfer. Table 3 also includes the corresponding free energies of transfer for $A_2 18C6$ [23] as representative of the crown ethers studied in this investigation. They demonstrate the insignificance of ligand solvation in comparison with that of Ag^+.

4.2. Complexes with monoaza-crown ethers

The stability constants, K_{11}, of 1:1 silver ion complexes with the monoaza-crown ethers in Table 1 vary over a wide range, between 10^3 and 10^{10} M^{-1}. Within a given solvent, however, the variation is much smaller. The alcohols and PC display an unquestionable maximum in log K_{11} for A18C6. This ligand offers a ring cavity size of estimated at 0.26 nm, which is optimally suited to accomodate a silver(I) cation, diameter 0.252 nm [33]. The diameters of A12C4 (0.12 nm) and A15C5 (0.17 nm) are too small, and that of A21C7 (0.34 nm) too large to embrace the silver(I) cation without an energy loss due to mis-adaption and steric strain. In the above, the diameters of the monoaza-crowns have been taken to be equal to the values estimated for the corresponding polyoxa-crown ethers [34], because the van der Waals volume of nitrogen (0.14 nm) [33] is almost identical to that of oxygen (0.15 nm). The complexation behaviour in these solvents is thus typical of that expected to result from the formation of inclusion complexes between the ligands and the silver(I) cation.

Unexpectedly, the log K_{11} values in DMSO and AN show no clear maximum and cannot be explained simply in terms of silver(I) ion solvation and ligand ring size. Superficially, this may suggest that the complex formed in these solvents are not inclusion complexes. A more detailed analysis of the results, including those for log β_{12} in Table 1 and the stability constants log K_{12}, for the second equilibrium, Eq. (3),

$$AgL^+ + L \overset{K_{12}}{\leftrightarrow} AgL_2^+ \tag{3}$$

obtained by combining Eqs. (1) and (2) (β_{12}/K_{11}), however, shows that this is not necessarily the case.

Two aspects of these results may be considered: the variation of all three constants with ligand size, and the ratio K_{11}/K_{12}. Fig. 1 shows the variations in stability constants with cavity diameter in methanol and ethanol, and the results show that β_{12} values are almost independent of cavity size, whereas K_{11} pass through a clear maximum at A18C6. The constant β_{12} values for $AgL_2{}^+$ formation are consistent with two monoaza-crown ligands acting as monodentate ligands with coordination through the nitrogen atoms in a manner analogous to that of the coordination geometry of silver(I) complexes with ammonia and aliphatic monoamines [7]. The equilibrium constant K_{12}, Eq. (3), shows

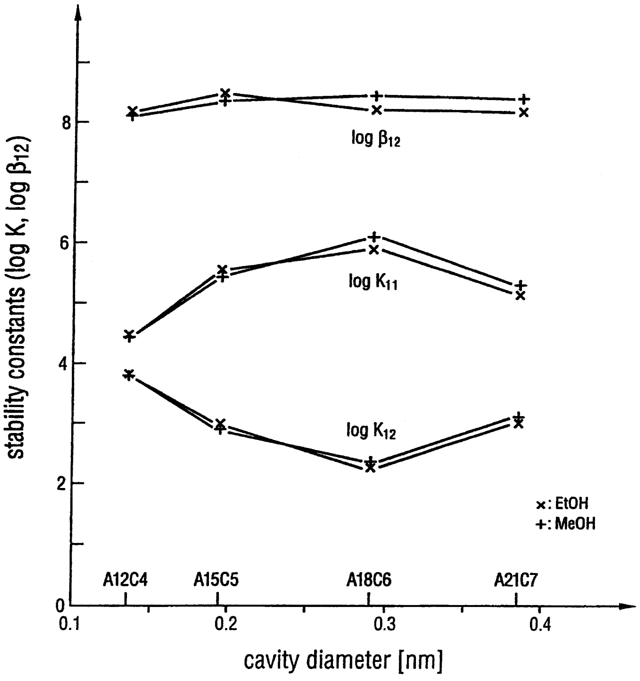

Fig. 1. Stability constants of 1:1 and 1:2 complexes of Ag^+ with monoaza-crown ethers in methanol and ethanol at 25 °C.

an inverse variation to that of K_{11} because the addition of the second ligand requires an accompanying transformation of the first-coordinated ligand from a polydentate to a monodentate ligand. This effort reaches a maximum when contacts of the ether oxygens in the $[Ag(A18C6)]^+$ inclusion complex have to be dissolved. Any effects of solvation of the ligands are expected to be independent of ring size because of the dominance of hydrogen bonding between the NH-group (and the nitrogen lone pair) of the ligands and the alcohols, and hence the overall stability constant β_{12} should be independent of ring size.

In the dipolar aprotic solvents a somewhat different picture is apparent, illustrated in Fig. 2 for the solvents DMSO, PC, and AN. A notable effect is the minimum in log β_{12} corresponding to A18C6 in all three solvents. There could be two contributing factors to this, a ring-size dependent solvation of the monoaza-crowns, and a ring-size conformational change associated with complex formation. It has been known for some time that 18C6 crystallises from AN as an 18C6–CH_3CN complex, which is used to purify the crown-ether [35]. In the association complex the protons of the methyl-group of CH_3CN are bonded to the ether oxygens and a change of ring size will disturb the optimal arrangement of these bonds. Since the replacement of an ether oxygen by a secondary amine nitrogen has an almost negligible effect on the ring size and conformational flexibility of a crown ether like 18C6 [18], it is reasonable to assume that monoaza-crown ethers of suitable size will also form association complexes with acetonitrile and other dipolar aprotic solvents with acidic C–H hydrogen atoms, such as DMSO. In AN, DMSO, and PC the log β_{12} values of the A12C4 complexes are always larger than those of the other complexes, the observed order of complex stability would suggest that the degree of association between the macrocycle and solvent increases in the order A12C4 < A15C5 ~ A21C7 < A18C6 (Fig. 2). There remains a question, however, whether these solvation effects would be large enough to account for the minima, given the results in Table 3, for example, which show that for A_218C6, there is very little difference in the solvation energies in AN, DMSO, and PC, and all are more weakly solvating than MeOH and EtOH with their ability to participate in hydrogen bonding. Another possibility is that in these aprotic solvents the lowest energy conformation of the free ligand is one in which the nitrogen lone pair is directed towards the interior of the cavity. Thus energy would be required in order to form AgL_2^+ complexes in which Ag^+ is external to the ligand cavity, interacting primarily with the nitrogen atom. The observed results would require that this process is most difficult for A18C6 and easiest for A12C4.

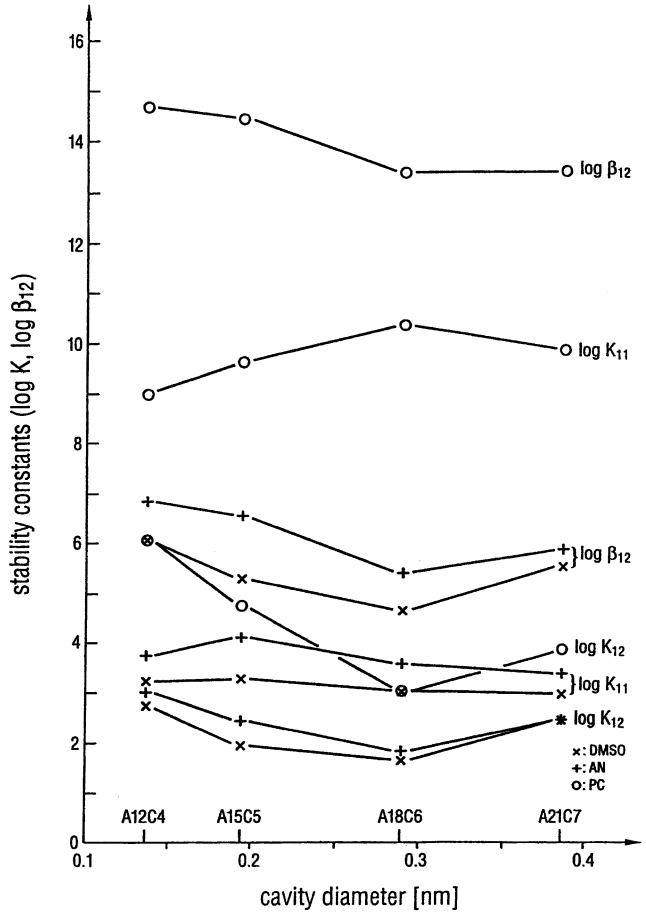

Fig. 2. Stability constants of 1:1 and 1:2 complexes of Ag^+ with monoaza-crown ethers in dimethylsulfoxide, acetonitrile and propylene carbonate at 25 °C.

The formation of an inclusive AgL^+ would be expected to show a maximum for L = A18C6, and while this is observed for complexes in PC, no such maxima are observed in DMSO and AN. The above factors related to ligand solvation and conformational effects would tend to mitigate against such a maximum, the former more particularly in DMSO and AN. An additional factor in DMSO and AN is that solvation of the complexed cation will be stronger the poorer the fit of the cation and cavity size and this will have a levelling effect on log K_{11} values for the different ligands (see below).

An additional factor which allow differentiation between monodentate and polydentate coordination of monoaza-crown ethers in AgL^+ complexes is the ratio of the stepwise stability constants, K_{11} and K_{12}. In complexation equilibria of monodentate ligands and a metal ion, when the maximum coordination number is two, purely statistical calculations lead to a ratio of $K_{11}/K_{12} = 4$ [36]. In real systems deviation from this value is common and is represented by a spreading factor x introduced by Bjerrum [37], such that $K_{11}/K_{12} = 4x^2$, in which x may vary between zero and infinity. The ratio $K_{11}/K_{12} = (K_{11})^2/\beta_{12}$, calculated from the results in Table 1, is listed in Table 4.

Table 4
Ratio of the consecutive stability constants, K_{11}/K_{12}, for AgL_2 complexes

Solvent, S	A12C4	A15C5	A18C6	A21C7
MeOH	3.5	4.3×10^2	5.4×10^3	1.6×10^2
EtOH	3.5	3.9×10^2	3.9×10^3	1.5×10^2
DMSO	3.3	2.2×10^1	2.9×10^1	2.8
AN	4.6	4.5×10^1	5.2×10^1	7.9
PC	3.7×10^2	7.9×10^4	1.9×10^7	9.1×10^5

The variation shown in Table 4 is impressive. The ratio K_{11}/K_{12} for the complexes of A12C4 is near the theoretical value of four for monodentate ligands in the alcohols and in the aprotic solvents which solvate Ag^+ strongly. The significant deviation of the factor x from unity (or the ratio ratio K_{11}/K_{12} from four) in PC indicates that in this solvent the ether–oxygen atoms of A12C4 in the 1:1 complex are involved in coordination of Ag^+. The coordination geometry of $[Ag(A12C4)]^+$ is, however, not typical of that expected for a inclusion complex, which has the ability to shield to varying degrees the cation from interactions with the solvent. The interior of A12C4 is small with respect to the size of Ag^+ and it tends, therefore, to act more like a normal polydentate ligand. The remaining larger ligands show clear evidence for inclusion complexes. The ratio K_{11}/K_{12} is normally larger than four, especially as the correspondence of the ring-cavity size and cation diameter increases, and the ability of the solvent to solvate the silver(I) ion decreases, reaching a striking 1.9×10^7 for A18C6 in PC. The low tendency of the solvent molecules to solvate the silver(I) ion in PC increases the tendency of the monoaza-crowns to form stable 1:1 complexes with Ag^+ in which all of the ligand donor atoms are brought into play. The lack of an observed maximum in $\log K_{11}$ in AN and DMSO reflects factors such as the solvation and conformational properties of the ligand, as discussed above. In addition, the increased solvation of complexed Ag^+ for complexes in which there is a mismatch between the cation and ligand-cavity size will also tend to even out the stability constants in these strongly solvating media. This point is considered more quantitatively below.

In summary, 1:1 complexes formed between Ag^+ and the monoaza-crowns are predominantly inclusion complexes with the possible exceptions of complexes of A12C4 where either the cation or the ligand donor atoms are well solvated, and complexes of the larger A21C7 in strongly Ag^+-solvating media such as DMSO and AN.

4.3. Complexes with diaza-crown ethers

The diaza-crown ethers may be taken as bidentate ligands in their complexes with Ag^+, because of the dominance of the interactions with the two nitrogen atoms compared with those of the oxygen-donor atoms, and they form almost exclusively 1:1 complexes. Only for $A_2$15C5 in PC we were able to obtain a value of K_{12} for AgL_2^+ formed in low amount in the presence of a large excess of ligand; the ratio K_{11}/K_{12} in this case is 1×10^{10}. The significance of the additional nitrogen atom compared with the monoaza-crowns is further emphasised by the observation that the $\log K_{11}$ values in Table 2 are some 10^2–10^5 times larger than for the corresponding complexes of Ag^+ with monoaza-crown ethers with the same number of ring atoms.

The overall variation of K_{11} in Table 2 between $10^{6.5}$ and $10^{15.5}$ is determined mainly by the solvent. Within a given solvent, however, the stability constant of the $A_2$18C6 complex is always the largest and exceeds those of the neighbouring diaza-crown ether complexes considerably (Fig. 3). The relative positions of the roof-like combinations of stability constants are determined predominantly by the strengths of the solvents with respect to solvating the silver(I) ion.

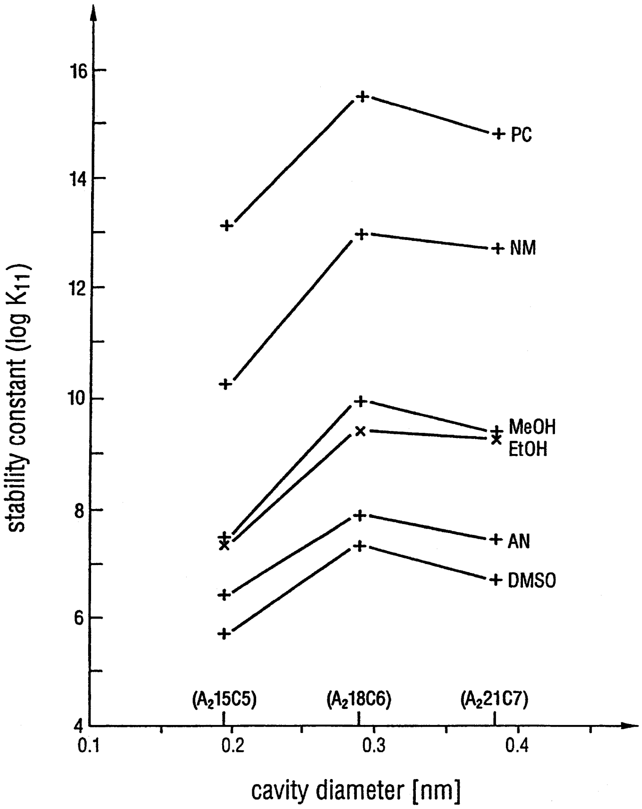

Fig. 3. Stability constants ($\log K_{11}$) of Ag^+ complexes with diaza-crown ethers in polar solvents at 25 °C.

4.4. A comparison of the stability constants of crown ethers with different combinations of oxygen- and nitrogen-donor atoms

When an ether–oxygen atom in a crown ether is replaced by an amine-nitrogen atom, the ring-cavity size is only very slightly influenced because the van der Waals radii of the two donor atoms are almost the same. In coordination equilibria with metal cations, the replacement of oxygen atoms by nitrogen atoms leads to a stability decrease for alkali metal cations, while for the corresponding silver(I) complexes, the stability constants are shifted by a similar magnitude but in the opposite direction. A compilation of stability constants of Ag^+ with various crown ethers in MeOH and PC is given in Table 5.

The dependencies of the stability constants on ring-cavity size are plotted in Figs. 4 and 5. In all cases, independent of the combination of oxygen and nitrogen atoms, the maximum value for log K_{11} is found for 18C6 and its derivatives. The dominant effect of the ligand nitrogen atoms on the aza-crowns is readily apparent, resulting in an increase in stability constant of almost nine orders of magnitude on going from 18C6 to $A_2$18C6 in PC. It is noticeable also that the stability increase per nitrogen atom is always larger in PC than in MeOH and this may reflect the increased interaction in the free ligand between the nitrogen atoms and methanol, compared with the oxygen atoms. The behaviour illustrated in Figs. 4 and 5 is typical of that expected for complexes in which the crown ethers are acting as polydentate ligands which tend to surround the silver(I) ion almost completely.

Table 5
Stability constants of 1:1 silver(I) complexes with polyoxa-, monoaza- and diaza-crown ethers in methanol and in propylene carbonate at 25 °C

Ligand, L	log K_{11} in MeOH	log K_{11} in PC
12C4	1.61 [a]	–
A12C4	4.34±0.01	8.62±0.09
$A_2$12C4	6.51 [b]	–
15C5	3.46±0.01; 3.59 [b]	6.24 [c]
A15C5	5.48±0.06	9.65±0.04
$A_2$15C5	7.49±0.01; 7.45 [d]	13.15±0.05
18C6	4.65 [e]	6.86 [c]
A18C6	6.08±0.04	10.31±0.07
$A_2$18C6	9.99 [f]	15.57 [f]
21C7	2.46 [g]	5.79 [c]
A21C7	5.27±0.01	9.81±0.05
$A_2$21C7	9.42±0.02 9.29 [d]; 9.60 [h]	14.92±0.03

[a] Ref. [38].
[b] Ref. [39].
[c] Ref. [40].
[d] Ref. [25].
[e] Ref. [41].
[f] Ref. [23].
[g] Ref. [42].
[h] Ref. [43].

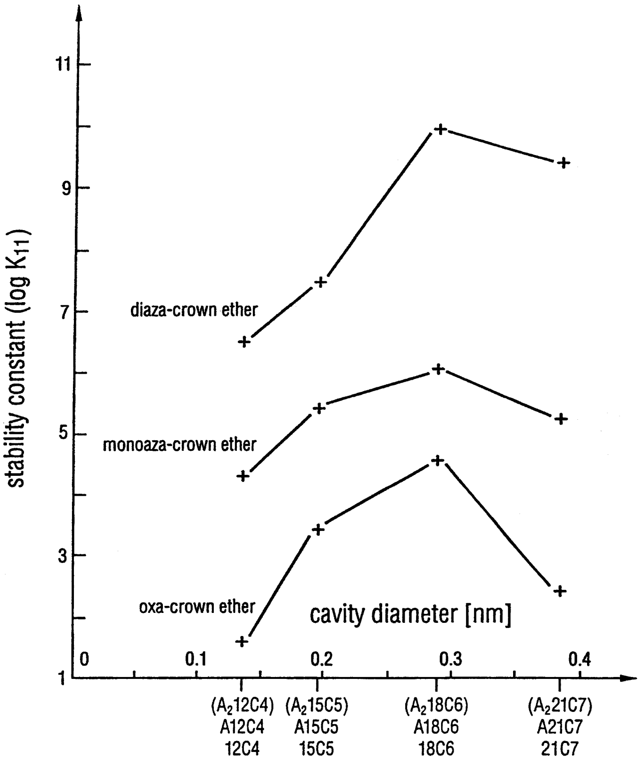

Fig. 4. Stability constants (log K_{11}) of Ag^+ complexes with aza-oxa-crown ethers different cavity diameters in methanol at 25 °C.

4.5. Solvation of the complexation components

The solvent dependence of the complex stabilities will depend upon the solvation of the components of the various equilibria involved. A relation between the stability constants and the free energies of solvation, ΔG_S, of silver(I) ion, the ligands, and the complexes involved in the equilibria can be derived using a thermodynamic Born–Haber cycle. The solvation free energies connect the equilibria of a given complexation process in vacuum (V) and in a solvent (S) and are related to the corresponding stability constants as follows,

$$-2.303RT \log(K^S_{AgL}/K^V_{AgL}) = \Delta G_S(AgL^+) - \Delta G_S(L) - \Delta G_S(Ag^+) \qquad (4)$$

If the analogous equation for another ligand L′ is substracted from Eq. (4), one obtains a relationship between experimentally accessible stability constants in solvent S,

$$\log K^S_{AgL'} = \log(K^V_{AgL'}/K^V_{AgL}) - \{\Delta G_S(AgL'^+) - \Delta G_S(L') - \Delta G_S(AgL^+) + \Delta G_S(L)\}/(2.303RT) + \log K^S_{AgL} \qquad (5)$$

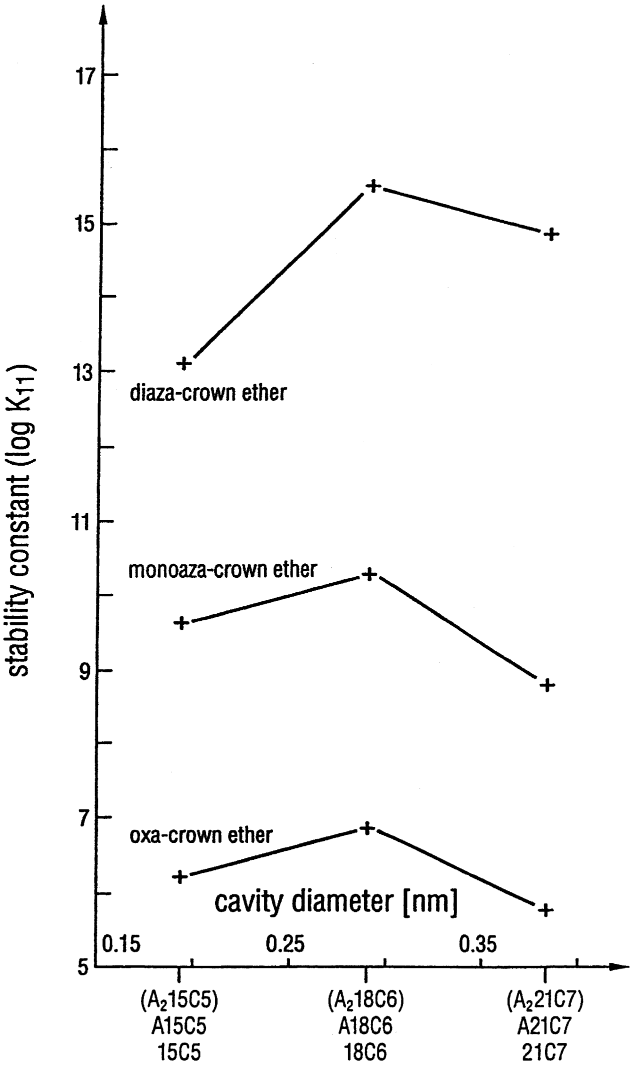

Fig. 5. Stability constants (log K_{11}) of Ag^+ complexes with aza-oxa-crown ethers of different cavity diameters in propylene carbonate at 25 °C.

Fig. 6 shows that the stability constants of Ag^+ with $L' = A_221C7$ are linearly dependent on the constants of complexes with $L = A_218C6$. Since the slope is one it follows from Eq. (5) that the second functional quantity on the right side is independent on solvent. Because of the very different solvent properties which spread out the stability constants of over seven orders of magnitude, and hence that the intercept on the y-axis corresponds to $\log(K^v_{AgL'}/K^v_{AgL})$, i.e. it is a measure of the ratio of the stability constants in vacuum. The result, reported in Table 6, means that in vacuum the silver(I) ion interacts equally with A_218C6 and A_221C7, and similarly for A18C6 with respect to A21C7. The parameters derived from the linear dependencies of the logarithms of stability constants for those pairs of ligands which exhibit a slope of unity are collected in Table 6.

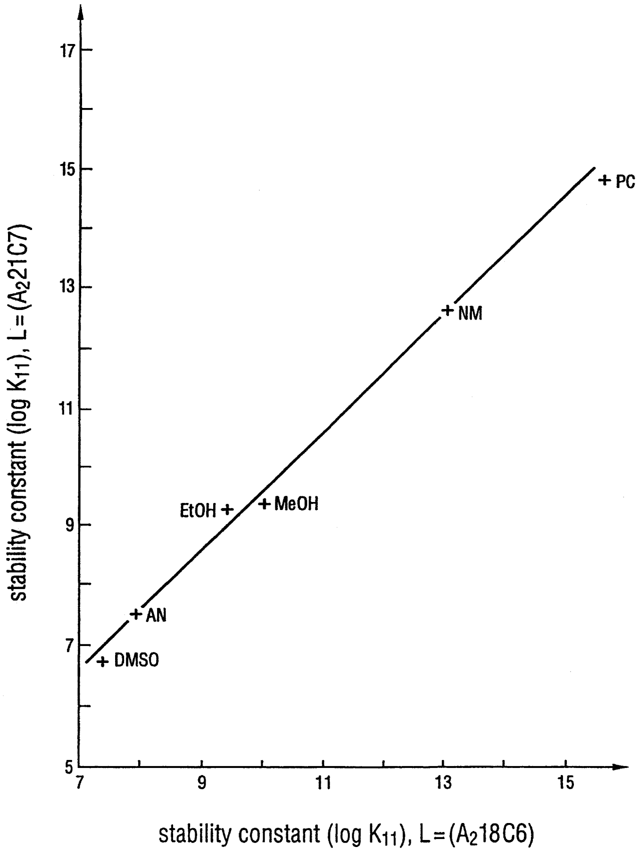

Fig. 6. Linear dependence of the stability constants (log K_{11}) of Ag^+ complexes with A_221C7 relative to those with A_218C6.

Table 6
Linear relations between stability constants of silver(I) complexes with different ligands (cf. Eq. (5))

$\log K^S_{AgL'} = m + n \log K^S_{AgL}$

L′	L	m	n
A_221C7	A_218C6	0.0 ± 0.2	0.97 ± 0.03
A21C7	A18C6	-0.3 ± 0.2	1.00 ± 0.03

$\log \beta^S_{AgL'_2} = m^* + n^* \log \beta^S_{AgL_2}$

L′	L	m*	n*
A21C7	A18C6	0.5 ± 0.2	1.0 ± 0.1
A15C5	A18C6	0.5 ± 0.2	1.0 ± 0.1
A12C4	A18C6	1.0 ± 0.8	0.98 ± 0.04

The corresponding linear relationship (Eq. (5)) for aza-crown ethers with less than 18 atoms in the ring, when combined with A_218C6 or A18C6, respectively, have slopes of less than 0.95—this shows, that the residual solvation of Ag^+ in the smaller crown ethers is different from that for the larger ones. It is also possible to derive from equilibrium (Eq. (2)) an equation analogous to Eq. (5) relating the overall stability constants $\beta^S_{AgL'_2}/\beta^S_{AgL_2}$ in solvent S. The slopes of all combinations of monoaza-crown ethers are near one (see Table 6), and supports the arguments given before that the monoaza-crown ethers act as monodentate amine-ligands with the silver(I) ion in AgL_2^+. The interceps indicate that in vacuum the silver(I) ion interacts somewhat less strongly with A18C6.

An alternative way to consider these results, which supports the above interpretations, is in terms of the relationship between the complexation equilibria in different solvents and the free energies of transfer of the species involved with respect to the reference solvent PC.

$$
\begin{aligned}
&-2.303RT\ \log(K^{S}_{AgL}/K^{PC}_{AgL}) \\
&\quad = \Delta G_{tr}(AgL^+;\ PC \to S) - \Delta G_{S}(L;\ PC \to S) \\
&\qquad - \Delta G_{tr}(Ag^+;\ PC \\
&\quad \to S) \qquad (6)
\end{aligned}
$$

The value of $\Delta G_{tr}(Ag^+; PC \to S)$ is tabulated in Table 3 and much larger than $\Delta G_{tr}(L; PC \to S)$, which is only known for a small number of cases (cf, Table 3). The other essential term in Eq. (6) is, therefore, the transfer free energy of the complex. Under favourable conditions, when the ligand shields the complexed cation completely from interactions with the medium, one finds that $\Delta G_{tr}(ML^+) \approx \Delta G_{tr}(L)$. Such behaviour is observed most often with cryptands in dipolar aprotic solvents, and in view of this the approximate identity of the transfer free energies of complexes and ligands is referred to as the cryptate hypothesis [44].

The transfer differences of silver(I) ion complexes with monoaza- and diaza-crown ethers, $\Delta G_{tr}(AgL^+) - \Delta G_{tr}(L)$, are listed in Table 7, together with those of the cryptand (2,2,2) for comparison. It is clear that even in the dipolar aprotic solvents studied there is no compensation of the transfer free energy terms of complexes with monoaza- and diaza-crown ethers and the ligands comparable to that found for cryptand (2,2,2). As might be expected, the closest similarity occurs for the larger diaza-crowns, which apparently shield the silver(I) ion quite effectively. Specific solvation effects for the ligands in the alcohols are apparently responsible for rather substantial positive free energy of transfer differences combination of the data in Tables 3 and 7 for $A_2$18C6 leads to free energy of transfer data of $[Ag(A_218C6)]^+$:$\Delta G_{tr}([Ag(A_218C6)]^+;\ PC \to S) = 16.1$ (MeOH), 19.0 (EtOH), −7.3 (DMSO) and 0.6 (AN) in kJ mol^{-1}. The complex $[Ag(A_218C6)]^+$ is less strongly solvated in the alcohols than in PC, since the electron donator atoms of the ligand are coordinatively bonded to Ag^+ and not involved in hydrogen bond formation with the alcohols.

Initially somewhat unexpected is the obvious cryptate-like behaviour of the 1:2 silver(I) complexes with monoaza-crown ethers in DMSO and AN (Table 8). The results are, however, quite consistent with the picture that the ligands coordinating as monodentate ligands in the AgL_2^+ complexes, a conclusion already reached explicitly from the variation of log β_{12} with ring-size and from slopes in Table 6. A comparison of the free energy of transfer differences for DMSO and AN in Table 8 with data for diaza-crown ethers in Table 7 shows that there is a difference between complexes in which the silver(I) ion is coordinated by two nitrogen atoms of the same ligand (e.g. diaza-crown ethers) and those in which the silver(I) ion is bound to the nitrogen atoms of two separate monoaza-ligands. In absolute values, $\Delta\Delta G_{tr}(AgL_2^+)$ of monoza-crown ethers is somewhat smaller than $\Delta\Delta G_{tr}(AgL^+)$ of diaza-crown ethers and more similar to $\Delta\Delta G_{tr}([Ag(2,2,2)]^+)$ in DMSO and

Table 8
Free energy of transfer differences $\Delta\Delta G_{tr}(AgL_2^+) = \Delta G_{tr}(AgL_2^+) - 2\Delta G_{tr}(L) = -2.303RT \times \log(\beta^{S}_{12}/\beta^{PC}_{12}) + \Delta G_{tr}(Ag^+)$ of 1:2 silver(I) complexes with monoaza-crown ethers at 25 °C (reference solvent: PC)

Solvent	$\Delta\Delta G_{tr}(AgL_2{}^+) = \Delta G_{tr}(AgL_2^+) - 2\Delta G_{tr}(L)$			
	A12C4	A15C5	A18C6	A21C7
MeOH	25.1	22.4	15.8	18.1
EtOH	23.3	20.1	15.5	17.4
DMSO	−3.9	−1.4	3.9	−6.9
AN	2.9	2.8	3.3	2.5

Table 7
Free energy of transfer differences $\Delta\Delta G_{tr}(AgL^+) = \Delta G_{tr}(AgL^+) - \Delta G_{tr}(L)$ of 1:1 silver(I) complexes with aza-crown ethers and (2,2,2) at 25 °C (Eq. (6), reference solvent: PC)

Solvent	$\Delta\Delta G_{tr}(AgL^+) = \Delta G_{tr}(AgL^+) - \Delta G_{tr}(L)$ [a]								ΔG_{tr} [a,b]
	A12C4	A15C5	A18C6	A21C7	$A_2$15C5	$A_2$18C6	$A_2$21C7	(2,2,2)	Ag^+
MeOH	12.2	11.6	12.0	13.7	20.1	19.7	19.2	11.4 [c]	−12.2
EtOH	10.5	10.0	11.3	12.6	19.1	21.2	18.2	13.6 [d]	−13.9
DMSO	−22.9	−17.4	−12.2	−14.5	−11.1	−6.9	−6.9	−2.1 [d]	−53.6
AN	−14.1	−10.3	−3.5	−5.3	−3.6	1.6	0.4	0.3 [d]	−42.0

[a] kJ mol^{-1}.

[b] Ref. [30].

AN. In the 1:1 complex of the silver(I) ion with diaza-crown ethers which are large enough to enclose the cation in the ring-cavity, the ethoxy-groups cannot shield the cation from interactions with the solvent as completely as is possible with cryptands. However, the extended ethoxy-portion of the monoaza-crown ethers prevents solvent molecules interacting directly with Ag^+ in the 1:2 complexes, even though the ether-oxygen atoms do not form coordinative bonds.

5. Conclusion

The stability constants of complexes between the silver(I) ion and monoaza- and diaza-crown ethers of different ring size are strongly dependent upon the solvent. The silver(I) ion forms 1:1 inclusion complexes with monoaza- and diaza-crown ethers of appropriate size, and the monoaza-crown ethers form additionally 1:2 (Ag^+:ligand) complexes, in which the monoaza-crowns act as simple monodentate ligands. In the latter complexes, the ligands shield the silver(I) ion from contact with the solvent much more effectively than the diaza-crown ethers in their inclusion complexes. A detailed analysis of the results in terms of free energies of transfer and solvation of the different species involved in the complexation equilibria shows that, in addition to the dominant influence of the solvation of the silver(I) ion, specific solvation of the free ligand or silver(I) complex can have a significant influence on the complex stabilities.

References

[1] J. Avraamides, A.J. Parker, in: R.R. Dogonadze, E. Kalman, A.A. Kornyshev, J. Ulstrub (Eds.), The Chemical Physics of Solvation, Part C, Elsevier, 1988.
[2] N.M.N. Gowda, S.B. Naikar, G.K.N. Reddy, Adv. Inorg. Chem. Radiochem. 28 (1984) 255.
[3] D.C. Luehrs, R.W. Nicholas, D.A. Hamm, J. Electroanal. Chem. 29 (1971) 417.
[4] S.E. Manahan, R.T. Iwamoto, J. Electroanal. Chem. 14 (1967) 213.
[5] L. Rodehüser, H. Schneider, Z. Physik. Chem., N.F. 100 (1976) 119.
[6] Y. Tsutsui, K. Sugimoto, H. Wasada, Y. Inada, S. Funahashi, J. Phys. Chem. 101 (1997) 2900.
[7] Gmelins Handbuch der anorg. Chemie, 8. Aufl., Silber, Part B6, Springer-Verlag, Berlin, 1975.
[8] R.M. Smith, A.E. Martell (Eds.), Critical Stability Constants, Amines, vol. 2, Plenum, New York, 1975.
[9] A. Thaler, N. Heidari, B.G. Cox, H. Schneider, Inorg. Chim. Acta 286 (1999) 160.
[10] A. Cassol, P. Di Bernardo, P. Zanonato, R. Portanova, M. Tolazzi, J. Chem. Soc., Dalton Trans. (1987) 657.
[11] L.E. Orgel, J. Chem. Soc. 4 (1958) 4186.
[12] G. Gritzner, Electrochim. Acta 44 (1998) 73.
[13] A.J. Parker, Adv. Phys. Org. Chem. 5 (1967) 17.
[14] C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, VCH, New York, 1988.
[15] E.J. King, in: A.K. Covington, T. Dickinson (Eds.), Physical Chemistry of Organic Solvent Systems, Plenum Press, London, 1973, p. 333.
[16] J.A. Riddick, W.B. Bunger, T.K. Sakano (Eds.), Organic Solvents; Physical Properties and Methods of Purification, fourth ed., Wiley, New York, 1986.
[17] E. Kauffmann, J.M. Lehn, J.P. Sauvage, Helv. Chim. Acta 59 (1976) 1099.
[18] T. Burchard, B.G. Cox, P. Firman, H. Schneider, Ber. Bunsenges. Phys. Chem. 98 (1994) 1526.
[19] B.G. Cox, J. Stroka, H. Schneider, Inorg. Chim. Acta 128 (1987) 207.
[20] H. Maeda, S. Furuyoshi, Y. Nakatsuji, M. Okahara, Bull. Chem. Soc. Jpn. 56 (1983) 212.
[21] N. Heidari, A. Thaler, B.G. Cox, H. Schneider, Inorg. Chim. Acta 279 (1998) 186.
[22] A. Thaler, B.G. Cox, H. Schneider, in preparation.
[23] B.G. Cox, P. Firman, H. Horst, H. Schneider, Polyhedron 2 (1983) 343.
[24] B. Spiess, F. Arnaud-Neu, M.J. Schwing-Weill, Helv. Chim. Acta 63 (1980) 2287.
[25] B.G. Cox, P. Firman, I. Schneider, H. Schneider, Inorg. Chem. 27 (1988) 4018.
[26] H.-J. Buschmann, Inorg. Chim. Acta 102 (1985) 95.
[27] B.G. Cox, J. Stroka, P. Firman, I. Schneider, H. Schneider, Aust. J. Chem. 36 (1983) 2133.
[28] M.C. Almasio, F. Arnaud-Neu, M.J. Schwing-Weill, Helv. Chim. Acta 66 (1983) 1296.
[29] K. Izutsu, M. Ito, E. Sarai, Anal. Sci. 1 (1985) 34.
[30] Y. Marcus, Ion Solvation, Wiley, Chichester, 1975.
[31] H.L. Friedman, C.V. Krishnan, in: F. Franks (Ed.), Water, A Comprehensive Treatise, vol. 3, Plenum Press, New York, 1973, p. 11.
[32] V. Gutmann, The Donor–Acceptor Approach to Molecular Interactions, Plenum Press, New York, 1978.
[33] L. Pauling, The Nature of Chemical Bond, Cornell University Press, New York, 1960.
[34] J.C. Pedersen, J. Am. Chem. Soc. 89 (1967) 7017.
[35] G.W. Gokel, D.J. Cram, C.L. Liotta, H.P. Harris, F.L. Cook, J. Org. Chem. 39 (1974) 2445.
[36] M.T. Beck, I. Nagypal, Chemistry of Complex Equilibria, Ellis Harwood, Chichester, 1990, p. 49.
[37] J. Bjerrum, Metal Amine Formation in Aqueous Solution, Haase, Copenhagen, 1941.
[38] J.R. Kaeffe, J. Morey, C.A. Palmer, J.C. Lee, J. Am. Chem. Soc. 101 (1979) 1295.
[39] H.-J. Buschmann, J. Solution Chem. 16 (1987) 181.
[40] J.C.G. Bünzli, F. Pilloud, Inorg. Chem. 28 (1989) 2638.
[41] H.-J. Buschmann, Chem. Ber. 118 (1985) 2741.
[42] J.D. Lamb, R.M. Izatt, S.W. Swain, J.J. Christensen, J. Am. Chem. Soc. 102 (1980) 475.
[43] H.-J. Buschmann, Inorg. Chim. Acta 102 (1985) 95.
[44] B.G. Cox, H. Schneider, Pure Appl. Chem. 61 (1989) 171.
[45] B.G. Cox, H. Schneider, J. Stroka, J. Am. Chem. Soc. 100 (1978) 4746.
[46] B.G. Cox, J. Garcia-Rosas, H. Schneider, J. Am. Chem. Soc. 103 (1981) 1384.