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Complex formation of silver(I) ion with some aminopolycarboxylate ligands

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Abstract

The complex formation of Ag^+ with iminodiacetate (IDA), nitrilotriacetate (NTA), 1,2-ethylenediamine-*N,N,N′,N′*-tetraacetate (EDTA), 1,3-diaminopropane-*N,N,N′,N′*-tetraacetate (TMTA) and 1,4-diaminobutane-*N,N,N′,N′*-tetraacetate (TETA) has been studied using potentiometric measurements at 25 °C and $I=1(KNO_3)$. The results obtained by different total concentrations of the components in the range 1×10^{-3} to 4×10^{-2} M are interpreted with formation of the following species: (a) IDA: AgHL, AgL^- and AgL_2^{3-}; (b) NTA: AgL^{2-}; (c) EDTA: $AgHL^{2-}$, AgL^{3-} and Ag_2L^{2-}; (d) TMTA: $AgHL^{2-}$, AgL^{3-}, $Ag_2L_2^{6-}$ and Ag_2L^{2-}; (e) TETA: $AgHL^{2-}$, AgL^{3-}, $Ag_2L_2^{6-}$ and Ag_2L^{2-}. In the case of the monoamine ligands the formation of AgL and AgL_2, found also for IDA but with $K_1>K_2$, is not respected by NTA for which only a 1:1 complex is obtained. The 1:1 complexes with 1,*n*-alkylenediamine ligands show weak stabilization by further chelation and an increased tendency for dimerization occurs by increasing the number of methylene groups between the two N atoms. EDTA and its homologs form also bimetallic Ag_2L^{2-} and protonated $AgHL^{2-}$ complexes in which their stabilities are dominated by the basicities of AgL^{3-} and HL^{3-}, respectively.

Introduction

Forty years ago, Bjerrum [1] reported that the Ag(I) ion forms complexes with ammonia and monoamines. They have a coordination number of two and are characterized by their linear N–Ag–N structure. When ethylenediamine (en) is used as a ligand, the steric strain accompanying the formation of the 1:1 chelate complex, to reach the above arrangement, impels an equilibrium with the open form. This latter leads to the formation of a dimeric ten-membered chelate ring $Ag_2en_2^{2+}$. These findings were first obtained in 1952 by Schwarzenbach *et al.* [2] (ionic strength $I=0.1$ M adjusted using $NaNO_3$, 20 °C), later improved by Ohtaki and Ito [3] ($I=3(LiClO_4)$, 25 °C) using new computational facilities allowing a detailed mathematical analysis of the experimental data and the simultaneous consideration of all possible complex species. Furthermore, the use of the ionic strength ($I=3(LiClO_4)$) allows a larger variation of the concentrations of the investigated reagents with respect to the case in which $I=0.1$. The experimental results obtained by Ohtaki and Ito allowed a more accurate determination of the stability constants of the species involved. These constants were similar to those of the previous paper, although the dimerization constant of $Agen^+$ (2 $Agen^+ \rightleftharpoons Ag_2en_2^{2+}$) was only $10^{2.2}$ instead of $10^{3.8}$. This discrepancy may be attributed to the different salt medium [4].

In the present work, the effect of introducing acetate groups to replace the hydrogen atoms in ammonia (NH_3) and amino groups ($-NH_2$) of some 1,*n*-alkyldiamines ($n=2$, 3 and 4) is discussed. The resulting ligands can coordinate not only through the nitrogen atom but through the oxygen atoms of the carboxylate groups as well. The case of glycine (HL) was investigated by Ohtaki *et al.* ($I=3(LiClO_4)$, 25 °C) [5] in which the variation of the silver and the ligand concentrations from 0.0025 to 0.020 M revealed the formation of $AgHL^+$ and $Ag(OH)L^-$ among the common complexes AgL and AgL_2^- in solution.

The investigated ligands are iminodiacetate (IDA), nitrilotriacetate (NTA), 1,2-ethylenediamine-*N*,*N*,*N′*,*N′*-tetraacetate (EDTA), 1,3-diaminopropane-*N*,*N*,*N′*,*N′*-tetraacetate (TMTA) and 1,4-diaminobutane-*N*,*N*,*N′*,*N′*-tetraacetate (TETA). In all five ligands, the investigations were carried out by largely varying the concentrations of the components involved, i.e. the silver ion and ligand at $I=1(KNO_3)$ and 25 °C using pH measurements with a glass electrode. This experimental method allows a fairly accurate determination of the equilibrium constants of the complex species formed. In this context, two questions are of particular interest;

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1. Is it possible to reduce the number of coordinate nitrogen atoms from two to one in a silver complex by increasing the number of available acetato groups in the ligand?
2. Are dimeric species Ag_2L_2 also present in solutions of silver ion and EDTA homologs?

Experimental

IDA (Fluka, purum) was recrystallized from water. EDTA, NTA and $AgNO_3$ (Fluka, puriss) were used without further purification. TMTA and TETA were synthesized by known procedures and controlled by elemental analysis [6]. The purity of all the ligands was verified by titration with standard carbonate-free KOH. Carbonate-free 0.1 and 0.5 M potassium hydroxide, adjusted to $I=1.00$ with KNO_3, were prepared from Merck Ampoules and standardized against pure dried oxalic acid. Nitric acid (E. Merck, reagent grade) was used without purification.

Equilibrium measurements

Potentiometric pH measurements were performed in a thermostated jacket, air tight 120 ml glass titration vessel fitted with a Philips GAH 110 glass electrode and a calomel (0.99 M KNO_3, 0.01 M KCl, $I=1.00$ M). The solutions were titrated under an atmosphere of N_2 gas which was purified and equilibrated with water vapor by passing through a 1.00 M KNO_3 solution. The system was kept at a constant temperature of 25.00 ± 0.01 °C by circulating thermostated water through the outer jacket of the vessel. All solutions to be titrated were adjusted to an ionic strength of $I=1.00$ M by addition of KNO_3. Measurements were carried out using an Orion Research 901 pH meter calibrated with standard strong acid at the same ionic strength 1.00 for $pH=-\log [H^+]$; $[H^+]$ being the known hydrogen ion concentration. The negative logarithm of the ionic product of water, pK_w, was calculated from the pH values of the strong base solutions. Small deviations in $pK_w \leq 0.02$ from the expected value (13.73 for 25 °C and $I=1(KNO_3)$ [7]) were assumed to be negligible, otherwise, the glass electrode was substituted by a new one.

Ligand protonation constants K_p of the anionic ligands $L^{\mu-}$ as defined by eqn. (1) are obtained by potentiometric titrations of solutions of the acid $H_pL^{(\mu-p)-}$.

$$H_{p-1}L^{(\mu-p+1)-} + H^+ \rightleftharpoons H_pL^{(\mu-p)-} \qquad (1)$$

$$K_p = \frac{[H_pL^{(\mu-p)-}]}{[H^+][H_{p-1}L^{(\mu-p+1)-}]}$$

Stability constants $\beta_{q,p,n}$ of the silver complexes expressed by equilibrium (2) are obtained by the corresponding titrations in the presence of silver ions. In order to ensure the obtainment of reliable constants

$$qAg^+ + pH^+ + nL^{\mu-} \rightleftharpoons Ag_qH_pL_n^{(n\mu-p-q)-} \qquad (2)$$

of each species, it is important to vary the total concentrations of Ag^+ and ligand by a factor of 4 (IDA, NTA, EDTA) to 10 (TMTA, TETA). We have used for the calculation of the equilibria with Ag^+ from 8 (NTA) to 17 (TETA) titration curves and the number of experimental points was from 165 (NTA) to 463 (TMTA). The calculation of the equilibrium constants K_p and $\beta_{q,p,n}$ was performed by use of the programs KONST and KVARI [8]. The quantity carrying the experimental error is the degree of neutralization g, i.e. the average number of protons neutralized per ligand. The constants are obtained by minimizing the sum of the differences between the experimental and calculated g values to reach a given pH value by varying the unknown constants. The hydrolysis of Ag^+ was taken into consideration using the value of $\log \beta_{1,-1,0} = -11.1$ [9]. The concentration of AgOH was always negligible (<0.0001 $[Ag]_t$).

Results and discussion

The alkalimetric titration curves of the acids $HNTA^{2-}$ and H_2EDTA^{2-} (0.004 M) alone and in the presence of an equimolar amount of Ag^+ are given in Figs. 1 and 2, respectively. As the complex formation with silver occurs in neutral and alkaline solutions, the initial solutions are already partially neutralized. This corresponds to solutions containing the following species; for IDA and NTA, HL^- and HL^{2-}, respectively and for diamine tetraacetic acids, H_2L^{2-}. In the case of NTA, the pH decrease due to complex formation by half neutralization of the acid is equal to 1.75. For EDTA, the same quantity is much smaller (0.6) by the first deprotonation but it increases to 3 in the second deprotonation showing that in this last case a larger stability constant should be expected if only 1:1 complexes are formed. The resultant equilibrium constants are given in Tables 1 and 2; for comparison, typical values with ammonia and glycine are included. The standard deviation of the degree of neutralization $s(g)$ is given as a measure of the reliability of the fit between the experimental and calculated curves using the constants obtained. The error in each constant given in parentheses represents three times the standard deviation and depends on the concentration of the corresponding species $[M_qH_pL_n]$ and increases with a decrease of the species concentration. Limit values are only given for constants in which upon their increase an increase in $s(g)$ occurs. The use of an inert salt often has an effect on the values of the constants

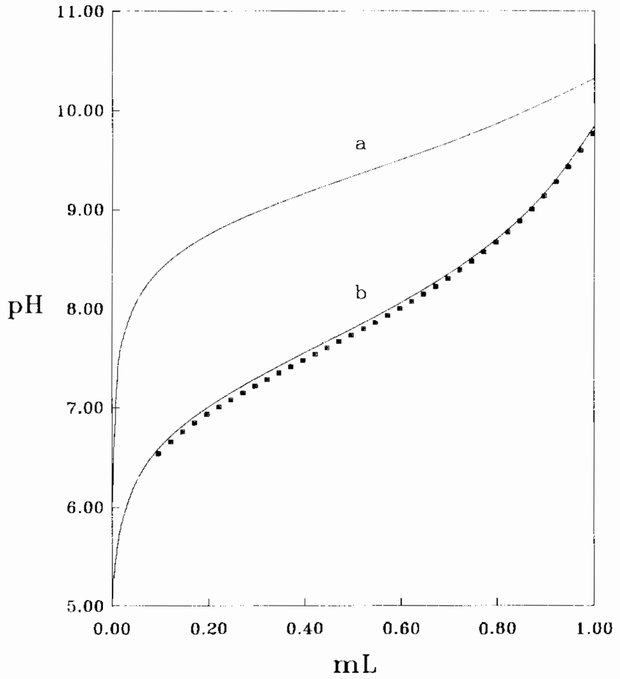

Fig. 1. Alkalimetric titrations of 100 ml of solutions containing: a, 0.004 M $HNTA^{2-}$; b, equimolar amounts (0.004 M) of $HNTA^{2-}$ and Ag^+ at $I=1(KNO_3)$ with 0.4 M KOH.

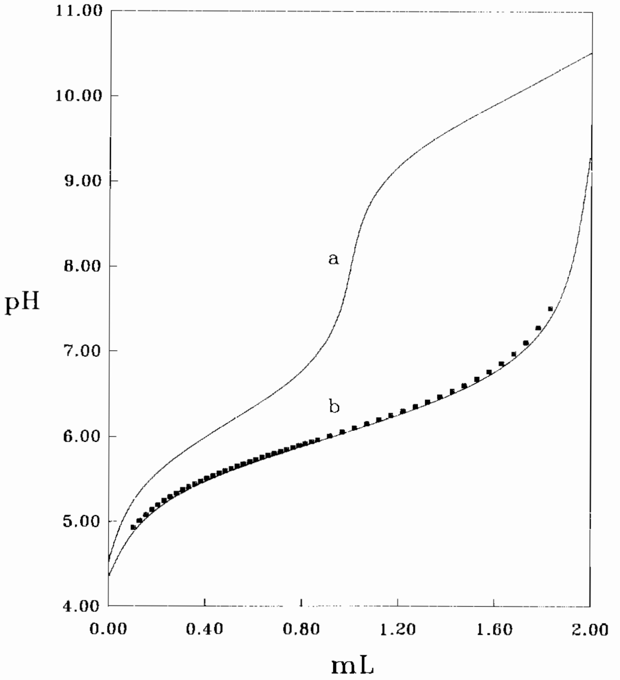

Fig. 2. Alkalimetric titrations of 100 ml of solutions containing: a, 0.004 M H_2EDTA^{2-}; b, equimolar amounts (0.004 M) of H_2EDTA^{2-} and Ag^+ at $I=1(KNO_3)$ with 0.4 M KOH.

measured if its ions associate with the species involved in equilibria. At $I=1(KNO_3)$ the investigated reacting species can form complexes or ion-pairs with potassium and nitrate ions. For the comparison of our values, we have to consider the interactions between the ligands and potassium ions, for which some values are already given in the literature [10] (see 8th column of Table 1 and 9th column of Table 2). In principle, for a given ligand, for instance EDTA, we have the possibility of potassium species with L^{4-}, HL^{3-}, H_2L^{2-}, ... Among the species, only those with the unprotonated ligand seem to be important. This is shown by the decrease of the value of log K_1 from 10.44 in $0.1((CH_3)_4NCl)$ to 10.24 in $0.1(KNO_3)$, whereas log K_2 is the same [11]. While discussing this change, we have to realize that two different effects are operative and causing the variation of K_1: (i) the change in the complexing cation concentration of the inert salt and (ii) the change in the ionic activity coefficients. If the I value is low, for instance 0.1, the ionic activity coefficients in two different salts will be very near and the variation of K_1 can be explained by complex formation, as in the above case of potassium. In this way, we have estimated the K_{KL} values [11] used here. The obtained $\beta_{q,p,n}$ are valid for the chosen medium and for comparison with literature data measured in the presence of non-complexing cations a correction is then necessary for the association with the cation M^{*+} of the inert salt. Indeed the free ligand $L^{\mu-}$ can be present as $M^*L^{(\mu-1)-}$ also, thus the non-bonded ligand will be given the symbol $[L^{\mu-}]_o$ instead of $[L^{\mu-}]$:

$$[L^{\mu-}]_o = [L^{\mu-}] + [M^*L^{(\mu-1)-}]$$

$$= [L^{\mu-}](1 + K_{M^*L}[M^{*+}])$$

$$[L^{\mu-}] = [L^{\mu-}]_o/(1 + K_{M^*L}[M^{*+}]) = [L^{\mu-}]_o/\Delta$$

This signifies that the equilibrium constants are obtained from $\beta_{q,p,n}$ multiplied by the term Δ raised to the power n. Although the values of K_{M^*L} are low, see Tables 1 and 2, the values of log Δ amount to 0.08 (glycine) upto 0.86 (EDTA).

The only literature value for NTA is that of Stary [12] (log $\beta_{1,0,1}=5.16$ ($I=0.1$ ($KClO_4$), 20 °C)) obtained by investigating the distribution of silver oxinate between chloroform and an aqueous NTA solution at different pH values. The given value corrected for K^+ association is log $\beta_{1,0,1}=5.16+0.14=5.30$, to be compared with our value $4.29+0.70=4.99$ at 25 °C. The difference between the two values can be explained by both the ionic strength and temperature, but the method of pH calibration is not mentioned in detail by Stary in order to ensure its reliability. In the case of EDTA, the values of Wikberg and Ringbom [13] ($I=0.1(KNO_3)$, 25 °C) are log $\beta_{1,0,1}=7.31+0.14=7.45$ and log $\beta_{1,1,1}=13.80+0.14=13.96$ in comparison with $6.50+0.86=7.36$ and $12.30+0.86=13.16$ in this work. The value of $\beta_{1,0,1}$ of EDTA is larger than that of en ($\beta_{1,0,1}=10^{5.06}$ [4]) in spite of the larger basicity of the latter ligand, showing

TABLE 1. Stability constants $\beta_{q,p,n}$ of the silver(I) complexes at 25 °C and $I=1(KNO_3)$. Ligand protonation constant K_1 and stability constant $K_{M\cdot L}$ of the complexes formed by the ligand with the cation of the inert salt; $s(g)$ standard deviation of the degree of neutralization

Ligand	log K_1	log $\beta_{1,0,1}$	log $\beta_{1,0,2}$	log $\beta_{1,1,1}$	log $\beta_{1,-1,1}$	$s(g)$	log $K_{M\cdot L}$	log Δ
NH_3[a]	9.40	3.30	7.21					
$NH_2CH_2COO^-$[b]	9.91	3.28	6.96	9.99	−6.48		−1.2[c]	0.08
$NH(CH_2COO^-)_2$	9.258	3.27(10)	5.90(20)	11.46(20)	≤ −8	0.016		
$N(CH_2COO^-)_3$	9.355	4.29(3)				0.005	0.6	0.7

[a] $I=2(NH_4NO_3)$. [b] $I=3(LiClO_4)$. [c] Ref. 9.

TABLE 2. Stability constants of the silver(I) complexes formed with EDTA homologs at 25 °C and $I=1(KNO_3)$. Ligand protonation constants K_1 and K_2 and stability constant K_{KL} of the complex formed by the ligand with potassium ion; $s(g)$ = standard deviation of the degree of neutralization (g)

Ligand	log K_1	log K_2	log $\beta_{1,1,1}$	log $\beta_{1,0,1}$	log $\beta_{2,0,2}$	log $\beta_{2,0,1}$	$s(g)$	log K_{KL}	log Δ
EDTA	9.80	6.167	12.30(10)	6.50(10)	≤ 13	7.60(50)	0.0058	0.8	0.86
TMTA	10.008	7.807	13.45(5)	5.02(15)	13.01(15)	8.22(8)	0.0146	0.4	0.54
TETA	10.195	8.881	14.10(7)	5.15(7)	13.70(15)	8.20(10)	0.0212	0.4	0.54

that the carboxylate groups are also involved in the coordination.

The data of Table 1 show that the successive introduction of CH_2–COO^- groups in ammonia is accomplished by a decrease in the value of $\beta_{1,0,2}$, in such a way that in the case of NTA only one ligand anion is bound by silver ion with participation of the carboxylate groups to the coordination. This corresponds to the exclusive formation of only one silver complex, which is characterized by a low value of $s(g)$. The increase of log $\beta_{1,0,1}$ for NTA is remarkable with respect to the values of the other ligands and by inclusion of the K^+ association. Because of the larger basicity of NTA (log $K_1=9.355+0.7=10.055$) with respect to NH_3 (9.40), a small part of it ($\simeq 0.25$ [1]) is due to this last effect. As already found with glycine, a protonated silver IDA complex is formed.

Protonated complexes have greater importance for the EDTA homologs; they are obtained in the solution of the monoprotonated ligand HL^{3-} in the presence of silver(I). The constant of eqn. (3) is identical to the ratio $\beta_{1,1,1}/K_1(=10^{2.5}$ (EDTA), $10^{3.5}$ (TMTA) and

$$Ag^+ + HL^{3-} \rightleftharpoons AgHL^{2-} \qquad (3)$$

$10^{3.9}$ (TETA)) and increases with the basicity of HL^{3-}, i.e. with K_2. As already found for other metal ions [14], the values of log $\beta_{1,0,1}$ decrease on going from a five-membered to larger chelate rings in spite of the larger increase of the ligand basicity measured by the sum log K_1 + log K_2. The values of the chelate effect Chel [15] measured by the difference log $\beta_{1,0,1}$ − log $\beta_{1,0,2}$ (IDA) is much lower (= 1.31) with respect to the values obtained by the other metal ions ($\simeq 4$ (Fe^{2+}, Co^{2+}, Ni^{2+})) [14]. This indicates the particular stereochemistry of the silver ion with preference for a linear structure. With TMTA and TETA the formation of dimeric 2:2 species is observed, for which the stability increases from TMTA to the more basic TETA. It appears that 2:2 species, as found by different ligands, forming the same ten-membered ring $Ag(NCCN)_2Ag$ [8, 16, 17] are also possible by larger rings. Similar 2:2 species with EDTA homologs have already been detected with Hg^{2+} [18] and the crystal structure of $Ba_2[Hg_2(TETA)_2]\cdot 14H_2O$ will be published soon [19]. In contrast with the other metal ions, and because of the low Chel values, all three homologs form 2:1 complexes Ag_2L^{2-}. The ratio of the stability constant of the 2:1 to the 1:1 complex is given by $[Ag_2L^{2-}]/[Ag^+][AgL^{3-}] = \beta_{2,0,1}/\beta_{1,0,1} = 10^{1.1}$ (EDTA), $10^{3.2}$ (TMTA) and $10^{3.05}$ (TETA). This large increase from EDTA to TMTA is due to the large increment of the basicity of AgL^{3-} (pK of $AgHL^{2-}$ = 5.80 (EDTA), 8.45 (TMTA). Further the above values for TMTA and TETA are similar to those expected for the coordination of iminodiacetate, thus indicating that in AgL^{3-} one iminodiacetate is mainly uncoordinated. The formation of 2:1 complexes M_2EDTA in solution has been observed with MoO_3 and WO_3 [20], because the coordination number of the metal center already bound to three oxygen atoms is reduced to three, which can be attained with coordination of one of the two iminodiacetate groups of EDTA. Further 2:1 complexes have been found with TETA [21] (Ca^{2+}, Mn^{2+}, Cd^{2+} and Pb^{2+}) and with higher homologs containing more than four methylene groups in the –N–N– chain [14]. In all these last complexes, their formation is possible because the chelated 1:1 complexes are not stabilized by a positive chelate effect [15].

Conclusions

(i) The exclusive formation of $AgNTA^{2-}$ shows that carboxylato groups are also quite effective as donors for silver(I).

(ii) The particular stereochemistry of silver(I) is responsible for the stoichiometries of the complexes formed by this cation with EDTA homologs. The formation of dimeric 2:2 TMTA and TETA complexes is a new result.

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