



## THE THERMODYNAMICS OF THE COORDINATION REACTIONS OF SILVER ION

### I—Complexes of $\text{Ag}^+$ with EDTA at pH 12

*The determination of Gibbs energy, enthalpy and entropy of the reaction between  $\text{Ag}^+$  and EDTA in aqueous solutions at constant pH (pH=12) has been carried out.*

*The equilibrium constant and the Gibbs energy have been obtained by measuring the concentrations of the silver ion in solution using a silver sulphide electrode. The enthalpy has been determined by a calorimetric method. The results show that the 1:1 complex is the only species formed at that pH.*

*The comparison of the values of the thermodynamic functions for this reaction with those available for reactions between  $\text{Ag}^+$  and nitrogen ligands indicates that the EDTA is bonded to the cation through the two N atoms and through some of its carboxylate groups.*

## 1 – INTRODUCTION

The complexation reactions of cations with amino-carboxylic acids have been the object of a number of studies. In part, interest in the study of these reactions stems from their extensive use in analytical chemistry. However, there is little literature data available on the silver ion with these ligands. In the only few detailed studies we know of on the reaction of  $\text{Ag}^+$  with ethylene-diaminetetra-acetic acid (EDTA), the equilibrium constant has been determined, in one case at three different temperatures [1–4].

The thermodynamics of complexation of silver with aminocarboxylic acids is of interest both from a structural point of view, and from the potential use of this reaction as an analytical method for determining  $\text{Ag}^+$ . In both cases there are many points which need clearing up. The enthalpimetric titration of  $\text{Ag}^+$  with EDTA has been reported by PRIESTLEY et al. [5, 6] as an analytical method which could be used for easy determination of the ion. However, the order of magnitude of the temperature variations found by these authors appears to us to be excessively high compared with the results of studies of the heat of the reactions with other cations. Further, we are doubtful about the formation of the complex species suggested in the explanation of the titration curve obtained.

As an electron acceptor the silver ion shows fairly different behaviour from the transition metal ions, those most studied in complexation reactions, such that results obtained for reactions of these cations cannot be generalized to the reactions of  $\text{Ag}^+$ .

In this work, a study has been made of the reaction of  $\text{Ag}^+$  with EDTA in aqueous solution at constant pH (pH=12), and from this the thermodynamic functions Gibbs energy, enthalpy and entropy have been obtained. At pH 12 the ligand is in tetrabasic form, which makes interpretation of the results simpler as it eliminates the possibility of having complexes involving protonated forms. However,  $\text{Ag}^+$  precipitates as the hydroxide at this pH and the free cation concentration is about  $5 \times 10^{-7}$  M [7], such that determinations can only be carried in solutions where there is an excess of EDTA. The equilibrium constant was determined by measuring the  $\text{Ag}^+$  concentration following addition of a known quantity of silver nitrate to an EDTA solution whilst the heat of reaction was measured using a calorimeter constructed in our laboratory specifically for this purpose.

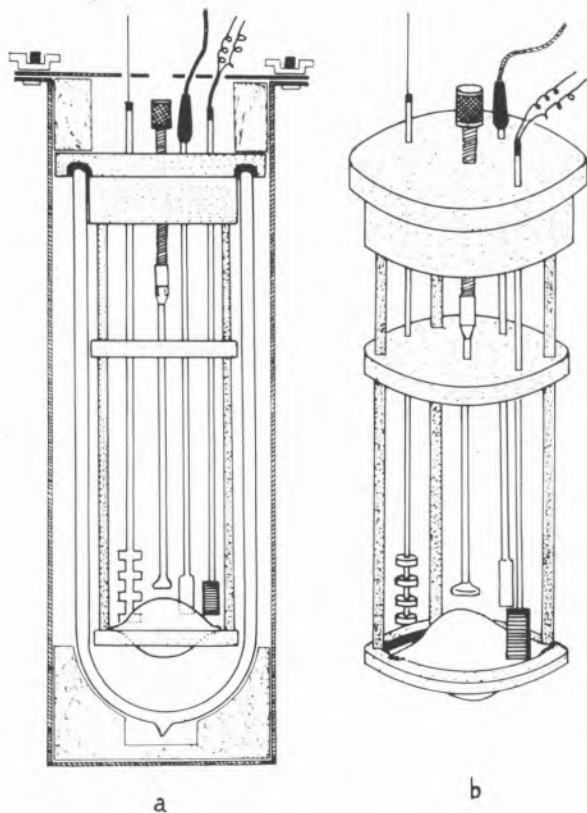


Fig. 1

- a) Schematic representation of the calorimeter  
b) Schematic view of the insert

## 2 – EXPERIMENTAL

The concentration of  $\text{Ag}^+$  in solution was determined by measuring the e.m.f. ( $E$ ) of a cell consisting of an ORION silver sulphide selective electrode and an  $\text{Ag-AgCl}$  double-junction reference electrode from the same firm. To samples of EDTA solutions of known concentration (0.001 to 0.08M) at pH 12, successive quantities of silver nitrate were added from a precision micrometer pipette, and the value of  $E$  was determined after each addition. Experimental conditions concerning the potentiometric measurements are described in a previous article[7]. The calorimeter was constructed from a silvered glass Dewar, with interior dimensions 18 cm deep by 5.5 cm wide, in which there was a structure consisting of two plexiglass discs, with a ring of the same material attached to it by ebonite rods. In this ring was fixed a glass ampoule containing one of the reagents. This structure acted as a support for the other components of the calo-

rimeter. The reagents were mixed by breaking the ampoule with a glass rod driven by a metal screw attached to the upper disc of the plastic frame.

The temperature variations were measured by a Hewlett-Packard model 2805A quartz thermometer, with which it is possible to study temperature changes of the order of  $10^{-4}^\circ\text{C}$ , corresponding, under the experimental conditions employed, to about 0.033 J.

Thorough mixing of solutions was ensured by using a glass stirrer with vertical movement attached to a variable speed electric motor kept at a speed of about 70 strokes per minute.

The Dewar flask inside a cylindrical copper can which was kept in a water bath thermostatted at  $25^\circ\text{C}$ . The upper disc, which acted as a cover to the Dewar had a rubber filled groove to fit it to the side of the flask and insulated it as far as possible. Two small pieces of cork were placed between the lid of the copper can and the upper plexiglass disc for holding the disc tight to the edge of the Dewar flask. The space between the lid of the can and that of the Dewar flask was filled with cotton waste for each experiment.

The EDTA solutions were prepared by adding potassium hydroxide to the dipotassium salt, adjusting the pH with the aid of a glass electrode. The silver nitrate solutions were prepared by weighing the pure salt. The water used in all experiments have been doubly distilled in all quartz apparatus.

$50\text{ cm}^3$  of EDTA solution was added to the Dewar flask, and 4 to  $5\text{ cm}^3$  of silver nitrate was introduced in a glass ampoule. This has been sealed with a glass-blowing torch and was fixed by its ends to the plexiglass ring in two small hollow mountings using a small amount of molten polystyrene. The quantity of silver nitrate used in each experiment was obtained from the concentration of the solution and the weight of the ampoule.

After setting up, the calorimeter was left during a night to ensure temperature equilibration. Stirring of the solution was started 30 to 60 minutes before initiation of the reaction, and the temperature was recorded 2 to 5 minute intervals. The temperature recording was continued for 15 to 30 minutes after mixing of reagents. To obtain the relationship between the observed temperature variations and the amount of available heat given to the calorimeter, after each reaction a known amount of heat was produced by passing an electric current across a constantan resistance of  $14.101\Omega$  which was isolated by cotton thread and protected by a thin

film of polystyrene. The current was produced by a lead battery, and its intensity determined by measuring with a Pye vernier potentiometer the drop in potential across a  $1\Omega$  standard resistance added to the heating circuit. The temperature variations following a calorimetric measurement are represented in fig. 2.

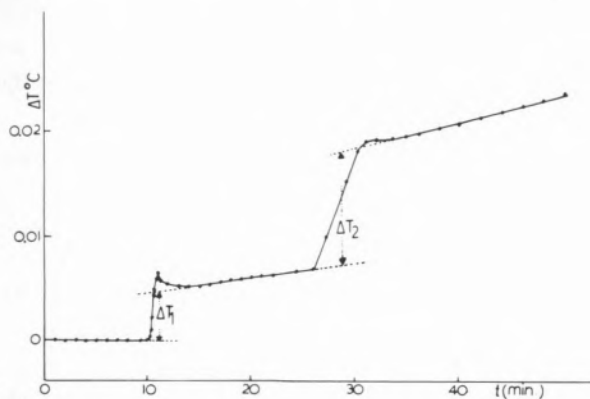


Fig. 2

Temperature variations during a calorimetric experiment.  $\Delta T_1$ , increasing of temperature due to the reaction;  $\Delta T_2$ , increasing of temperature due to the input electrical energy

### 3 - RESULTS

The values of  $E$  as a function of the total concentration of added  $\text{Ag}^+$  are shown in fig. 3. The calibration curves for obtaining the correspondence between  $E$  values and the silver ion concentration were obtained by adding successive quantities of silver nitrate solution to a known volume of potassium nitrate solution, whose concentration was determined from the claimed ionic strength.

The calibration graphs show a linear variation of  $E$  with  $\log [\text{Ag}^+]$  to concentrations of the order  $10^{-6}\text{M}$ , with slope  $59.2\text{ mV}$ , the value expected from the Nernst equation. The  $E$  values for concentrations lower than  $10^{-6}\text{M}$ , i.e. below the linear part of graphs, were obtained by extrapolating the lines defined by the experimental values. The experimental results shown in fig. 3 indicate that the extension of the lines  $E$  against  $\log [\text{Ag}^+]$  is reasonable to concentration values of the order  $10^{-5}\text{M}$ . Below this value irregularities in the response of the selective electrode start to be observed.

The results obtained for the enthalpy of reaction are given in Table I.

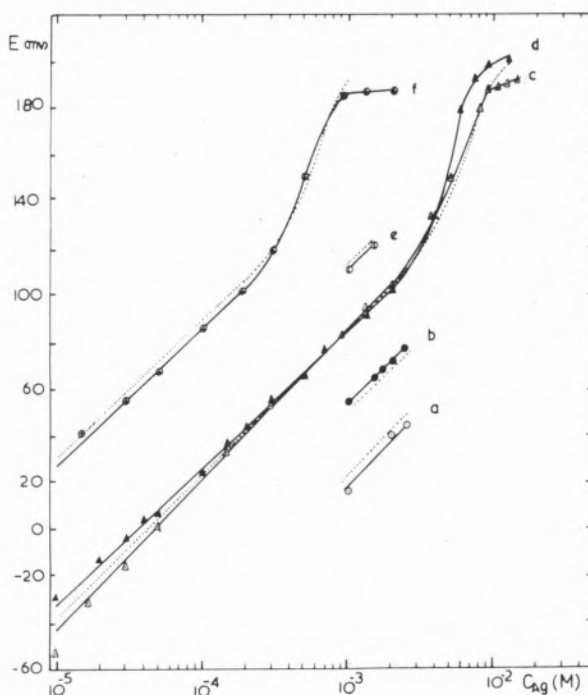


Fig. 3

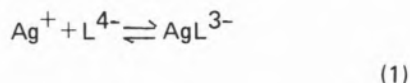
$E$ , m. f. of the cell as a function of the total silver concentration for different values of ligand concentration. Concent. of ligand: a)  $8.7 \times 10^{-2}$ ; b)  $4.4 \times 10^{-2}$ ; c)  $10^{-2}$ ; d)  $10^{-2}$ ; e)  $4.4 \times 10^{-3}$ ; f)  $10^{-3}\text{ M}$ . Dotted lines are the graphical representation of equ. (4).

Table I  
Enthalpies of reaction of  $\text{Ag}^+$  with EDTA

Conc. of EDTA/mM	Conc. of $\text{Ag}^+$ /mM	$-\Delta H/\text{kJ mol}^{-1}$
9.3	0.91	25.19
8.6	0.91	26.78
10.3	1.35	25.15
7.6	0.92	23.39
8.5	1.37	22.72
9.2	1.83	23.56
8.2	1.83	23.51
7.7	2.31	23.01
9.1	2.27	21.97
8.6	2.74	20.96
7.0	1.86	24.89
8.2	2.29	26.69
9.4	3.17	23.26
8.0	2.76	24.77
9.7	3.61	21.59

## 4 - DISCUSSION

In analysing the results, the first point which has to be considered is the type of complexes formed. As in the pH region studied excludes the possibility of formation of protonated compounds, so, we are going to assume that only complexes present in solution are of the 1:1 type, i.e. those resulting from the reaction



Where  $L$  represents EDTA

Now, the total added  $\text{Ag}^+$  concentration,  $C_{\text{Ag}}$ , and the total ligand concentration,  $C_L$ , are related to the concentrations of these species present in solution by the following equations

$$C_{\text{Ag}} = [\text{Ag}^+] + [\text{AgL}^{3-}] \quad \text{and} \quad C_L = [\text{L}^{4-}] + [\text{AgL}^{3-}]$$

From these two equations we can derive the following relationship

$$\frac{C_{\text{Ag}}}{[\text{Ag}^+]} = \frac{1 + K (C_L + [\text{Ag}^+])}{1 + K [\text{Ag}^+]}$$

where  $K$  is the stability constant of the complex formed in reaction (1) if the activity coefficients of the species are neglected.

As the  $\text{Ag}^+$  concentration in the solutions studied varies between  $10^{-11}$  and  $10^{-7}$  M, always  $C_L \gg [\text{Ag}^+]$ , and as  $K C_L \gg 1$ , the previous expression can take the form

$$\frac{C_{\text{Ag}}}{[\text{Ag}^+]} = \frac{K C_L}{1 + K [\text{Ag}^+]} \quad \text{or} \quad [\text{Ag}^+] = \frac{C_{\text{Ag}}}{K (C_L - C_{\text{Ag}})} \quad (2)$$

The values of  $E$  are related to the  $\text{Ag}^+$  concentration in solution by an expression of the type

$$E = C + \frac{RT}{F} \ln [\text{Ag}^+] \quad (3)$$

in which  $C$  includes the potential of the reference electrode, the formal potential of the selective electrode, and the junction potentials present in the cell. Introducing the values of  $\text{Ag}^+$  concentration given by (2) to equation (3), we obtain the relationship between  $E$ ,  $C_L$  and  $C_{\text{Ag}}$

$$E = C - \frac{RT}{F} \ln K - \frac{RT}{F} \ln (C_L - C_{\text{Ag}}) + \frac{RT}{F} \ln C_{\text{Ag}} \quad (4)$$

Equation (4) suggests that a graph of  $E$  as a function of  $\log C_{\text{Ag}}$  will give a straight line of slope 59.2 mV, since  $C_{\text{Ag}} \ll C_L$  and  $K$  remains constant. This is verified experimentally in the graphs of fig. 3 where  $C_{\text{Ag}} / C_L < 0.1$ . Equation 4 also suggests that when  $C_{\text{Ag}}$  and  $K$  are constant,  $E$  varies linearly with  $\log (C_L - C_{\text{Ag}})$ , with the line having a slope of -59.2 mV.

In fig. 4 results for  $E$  against  $\log (C_L - C_{\text{Ag}})$  are shown for  $C_{\text{Ag}}$  values of  $5 \times 10^{-5}$ ,  $10^{-4}$ ,  $5 \times 10^{-4}$ ,  $10^{-3}$  and  $5 \times 10^{-3}$  M. The graphs are in fact linear, and least squares analysis of the lines gives slopes varying between 60 and 64 mV. The big scatter of the points in this case relative to fig. 3 possibly arises from the fact that, in this case, the results correspond to readings in which successive quantities of silver nitrate have been added at different times, and so are more subject to errors. Apart from this, small deviations of slopes relative to those predicted by equation (4) may result from the fact that each line does not correspond to a constant ionic strength.

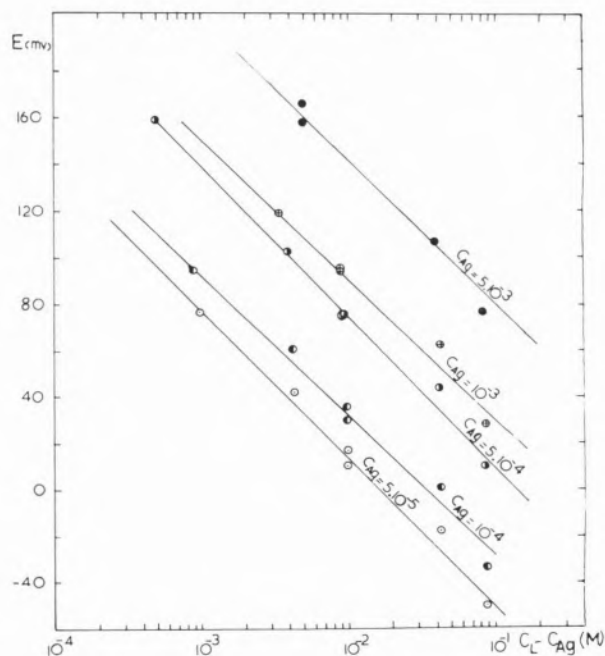


Fig. 4  
 $E$  against  $C_L - C_{\text{Ag}}$  for different values of total silver concentration



The stability constant, neglecting activity coefficients, is given by the expression

$$K = \frac{[AgL^{3-}]}{[Ag^+][L^{4-}]}$$

Given the fact that in the presence of an excess of EDTA there is no formation of complexes of  $Ag^+$  with  $OH^-$ , and that  $K$  has a high value, the previous expression can be replaced by

$$K = \frac{C_{Ag}}{[Ag^+](C_L - C_{Ag})}$$

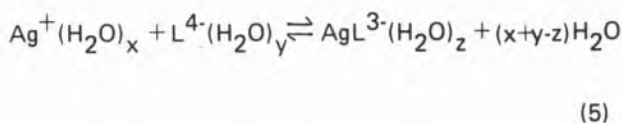
This was the form used for calculating this constant. The value calculated for  $K$ , taking the average of the values obtained for  $C_{Ag} = 5 \times 10^{-5}$ ,  $10^{-4}$ ,  $5 \times 10^{-4}$ ,  $10^{-3}$  and  $5 \times 10^{-3}$  M is equal to  $(1.12 \pm 0.15) \times 10^7$ .

In fig. 3 are shown the theoretical curves calculated from equation (4) using the value of  $K$  quoted above. The approximation of these curves to those obtained experimentally can be noted, suggesting that the equation provides a fairly satisfactory fit to the experimental results. There appears little doubt, therefore, that the only complex formed is  $AgL^{3-}$ . This conclusion is in agreement with that which can be drawn from the enthalpy results, where these are shown to stay constant when  $C_{Ag}/C_L$  is varied between 0.1 and 0.37.

The following results are calculated for the thermodynamic functions:  $\Delta G = -39.7 \pm 0.1$  kJ mol $^{-1}$ ,  $\Delta H = -23.8 \pm 0.4$  kJ mol $^{-1}$  and  $\Delta S = 53.0 \pm 1.7$  J mol $^{-1}$  K $^{-1}$ . We are not aware of any published data for the heat of this complexation reaction. However, it is possible to calculate a value from the data for equilibrium constants at 15, 25 and 35 °C determined by RECHNITZ e col. [4]. From the results of this group, the following values are calculated:  $\Delta G = -41.54$  kJ mol $^{-1}$ ,  $\Delta H = -17.56$  kJ mol $^{-1}$ , and  $\Delta S = 80.5$  J mol $^{-1}$  K $^{-1}$ . The enthalpy value is rather different from that obtained in the present study. However, this must arise in part from the lower precision inherent in calculating  $\Delta H$  from the temperature dependence of the equilibrium constant compared with direct calorimetric measurement.

It is clear that the value of each of the thermodynamic functions reflects not just the interaction between the cation and ligand, but also the loss of water from these

species which occurs in the reaction. This process can be represented in the following form



The bonding between  $Ag^+$  and EDTA leads to the liberation of a certain number of molecules of water owing to the decrease in the surface available for their fixation, and a weakening of the interaction forces of all or part of these molecules which are kept in the hydration sphere of the complex as a result of the partial neutralization of the electrical charge. Both of these effects give a positive contribution to the enthalpy and entropy whilst the bonding between the cation and ligand provides a contribution of the opposite sign.

The impossibility of measuring each of these contributions separately constitutes a major limitation to the analysis of the thermodynamic parameters of the reactions occurring in solution. However, some important conclusions can be drawn both from direct analysis of the results, and from a comparison with results from reactions with other ligands or cations.

In spite of the effect of complex formation — evidenced as we saw from the entropy value — the enthalpy of the reaction is fairly low, showing the presence of a strong interaction between  $Ag^+$  and EDTA. The enthalpy contribution to the complex stability is bigger than that of the entropy.

The entropy is a function which allows a simpler analysis, leading to a greater number of conclusions. This must result from the fact that it is more sensitive to the number of species (ions and water molecules) that are bonding or separating during the reaction than to the value of the forces involved in the bonding. The first conclusion which comes from the relatively high  $\Delta S$  value is the importance of the loss of hydration of species forming the complex, which exceeds the effects resulting from bonding between cation and ligand.

Further, from the entropy variation it is possible to elucidate some aspects of the structure of the complex formed. Given the softer character of nitrogen relative to oxygen, it is probable that the strongest bond between  $Ag^+$  and EDTA is to this atom. However, since the experimental results show that the combination ratio is one silver ion to one EDTA molecule and that no polynuclear complexes exist, it can be assumed — considering that

the two nitrogen atoms are situated in equivalent positions in the EDTA — that the silver ion is bonded to the molecule through these two atoms.

To extend the study of the structure of the complex it is of interest to compare the entropy of the reaction studied in this work with that of reactions in which  $\text{Ag}^+$  combines with ligands in which the only donor atom is nitrogen. We have found literature data for reactions with the following compounds: ammonia, pyridine, pyrazine, piperidine and 2,2-bipyridyl [8–12]. For all these reactions  $\Delta S$  has a negative value. If the bonding between  $\text{Ag}^+$  and EDTA was only through the two nitrogen atoms the entropy of the complexation reaction would be expected also to be negative, and the same order of magnitude as in the reaction with the above ligands. However, in fact the entropy of the reaction with EDTA is positive and relatively high, showing that in this reaction there is liberation of a greater number of water molecules than in the case of ammonia or the heterocyclic nitrogen compounds. The hydration of ammonia and the other nitrogen compounds is weak, as has been shown for primary amines where only one water molecule is bound to the nitrogen atom with any appreciable force [13]. We do not know of any data on the hydration of EDTA molecule. However, it is known that acetate ion, in spite of its size, exerts an appreciable interaction on the water, as shown for example by the large  $B$  value in the viscosity equation for ionic solutions [14]. Since EDTA has 4 acetate groups, its hydration must be important bearing in mind the water molecules bound to these groups.

The fact that a greater liberation of water molecules is found with EDTA than with ligands just having nitrogen as coordination centre appears to suggest that it comes in part from acetate groups which are involved in the bonding with  $\text{Ag}^+$ . The coordination number of the complex must then be greater than 2, which is known to be the smallest coordination number of the silver ion in its complexes with nitrogen and similar atoms. However, coordination numbers greater than 2, particularly 4, have been considered in complexes of  $\text{Ag}^+$  with ligands which can give  $\pi$ -bonding [15].

In addition the fact that EDTA has 6 electron donor centres favours formation of a structure in which the coordination number is bigger than that which would be found with ligands which only have one or two donor centres. It seems likely, therefore, that we can conclude in the complex of  $\text{Ag}^+$  with EDTA the bonding takes place

through the two nitrogen atoms and a number, probably 2, of the carboxylate groups of the ligand, leading to a tetrahedral structure.

It is curious to note, though, that the  $\Delta S$  value for the reaction of  $\text{Ag}^+$  with EDTA is still higher than that expected on the basis of the cation hydration. Indeed, plotting the  $\Delta S$  value obtained for this reaction with those published for the reaction of EDTA with other cations [16] as a function of the entropy of hydration of the cations [17] shows that the majority of these results lie on a straight line (fig. 5). The results for Zn and Cu lie just above this line. However, the data for Hg, Pb and Ag show rather more scatter, with the biggest deviation being shown by this last ion.

Such behaviour for  $\text{Ag}^+$  is unexpected. However, as the ligand is the same in all the reactions considered a higher  $\Delta S$  value than predicted from hydration of the corresponding cation can be explained by the following possibilities: liberation of a relatively bigger number of molecules of water of hydration of the cation, smaller entropy of hydration of the complex formed, or bigger entropy of formation of the complex without inclusion of the effect of hydration.

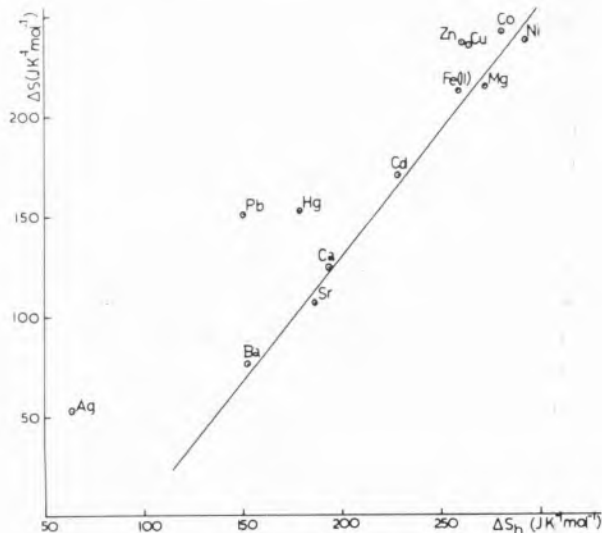


Fig. 5  
Entropy of reaction with EDTA against entropy of hydration of the corresponding cations

We cannot expect that the number of water molecules bonded to the complex of  $\text{Ag}^+$  with EDTA is less than that of other cations, many of which have bigger coordination numbers and a stronger interaction with EDTA,

therefore it would not be possible to observe a relative removal of more molecules of water of hydration or a bigger entropy of hydration of the complex. The remaining hypothesis is that the high  $\Delta S$  value obtained comes from a bigger entropy of formation. Cobble [18] came to the conclusion that the formation of each ring in a polydentate complex accounted for an entropy difference of ca  $58,5 \text{ J mol}^{-1} \text{ K}^{-1}$ . If we consider that many of the cations in the graph of fig. 5 give EDTA complexes with bigger coordination numbers than  $\text{Ag}^+$ , we can attribute the bigger entropy of formation of this complex to the fact that fewer rings are formed here. This idea is in agreement with a tetrahedral structure for the complex of  $\text{Ag}^+$  with EDTA, in contrast to the complexes with transition metal ions which are normally octahedral.

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## RESUMO

Neste trabalho fez-se a determinação dos valores das funções termodinâmicas energia de Gibbs, entalpia e entropia da reacção do  $\text{Ag}^+$  com EDTA em soluções aquosas de  $\text{pH}=12$ . Os valores da constante de equilíbrio e da energia de Gibbs foram obtidos medindo a concentração do ião prata em solução por meio de um eléctrodo selectivo de sulfeto de prata. A entalpia foi determinada por medidas calorimétricas. Os resultados obtidos mostram que para aquele valor de  $\text{pH}$  o único complexo que se forma em solução é do tipo 1:1. Da comparação dos valores das funções termodinâmicas obtidos para a reacção estudada neste trabalho com os obtidos por outros autores para as reacções entre o  $\text{Ag}^+$  e ligandos em que os únicos átomos electrodadores são átomos de azoto, conclui-se que a molécula do EDTA se liga ao  $\text{Ag}^+$  através dos dois átomos de azoto e de alguns dos seus grupos carboxílicos.