

Fig. 3. Influência do cromato na intensidade do pico de Zn(II), em função do tempo (Técnica ASV).

Pela análise dos resultados obtidos concluímos que há formação de duas novas espécies na solução. Uma eletroativa, que causa o decaimento da corrente, e a outra eletroativa, caracterizada pelo aparecimento do 2º pico.

As experiências foram realizadas utilizando-se o conjunto polarográfico da PAR, reagentes da Merck (Suprapuro ou P.A) e água "quartex"(7).

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## THE USE OF ION SELECTIVE ELECTRODE IN THE STUDY OF COMPLEX FORMATION. REACTIONS OF SILVER ION WITH AMINO AND CARBOXYLIC GROUP LIGANDS.

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### INTRODUCTION

Some of the ion selective electrodes commercially available allow the measurement of ionic activities in solution in a large range concentrations and with very high precision. The detection limits are  $10^{-6}$  -  $10^{-7}$  mol. dm<sup>-3</sup>, much lower than those reached by metallic electrodes. Furthermore the electrode equilibrium is quickly obtained. These features make the use of selective electrodes successful for measuring ionic activities in the study of complexation reactions. Actually in these reactions it is important to sweep from a high to a low range of concentration. This is the only way to put in evidence a larger number of formed species.

Nevertheless the application of these electrodes in complexing media basically raise two questions<sup>1,2</sup>: the first concerns the possibility of making measurements of concentration values below the limit of the experimental calibration curve; the second concerns the interference of the complexing agent on the equilibrium of the electrode.

In this paper we present the results obtained with the silver sul-

phide selective electrode, in the determination of the silver ion concentration in the study of silver complexes with ligands that contain amino and carboxylic groups.

#### EXPERIMENTAL

To ligand solutions successive quantities of standard solutions of silver ion were added. The concentration of silver ion in the solution being determined with an Orion Ag<sub>2</sub>S electrode and double junction Ag/AgCl electrode as reference.

To determine the silver concentration from emf values, a calibration curve was made by adding successive quantities of silver to a 0.1 mol.dm<sup>-3</sup> KNO<sub>3</sub> solution.

The electrode's response is nerstian to concentrations to the order of 10<sup>-7</sup> mol.dm<sup>-3</sup>.

The ligands studied were ethylenediamine (EN), diethylenetriamine (DIEN), glycine (GLY), iminodiacetic acid (IDA) and nitrilotriacetic acid (NTA).

#### RESULTS

The stability constants of the complexes formed were calculated from the total concentration of silver  $C_{Ag}$ , ligand  $C_L$  and  $Ag^+$  in solution, using the computer program Miniquad<sup>3</sup>.

The values obtained for the stability constants of the species formed for each system as well as experimental conditions are found in the Table I.

Results show that the relation between emf and the ion silver concentration, confirmed experimentally to a concentration of 10<sup>-7</sup> mol.dm<sup>-3</sup> ( $E = 551.4 + 59.18 \log [Ag^+]$ ), can be used for determinations of concentration of this ion as low as 10<sup>-10</sup> mol.dm<sup>-3</sup>, provided the total ion concentration is greater than 10<sup>-6</sup> mol.dm<sup>-3</sup> (Fig. 1). The precision found for the equilibrium constants determined in this way pointed out the good precision on the silver ion measurements.

Furthermore, the direct measuring process of the silver ion concentration leads to more confident results with respect to the formed

Table I - Complex formation of the silver ion with several ligands at 25°C and  $\mu = 0.1$  mol.dm<sup>-3</sup>.

| Ligand (L) | concentration range                         |                                           | Ag <sup>+</sup><br>(mol.dm <sup>-3</sup> )   | species<br>in solution                       | log stability<br>constant |
|------------|---------------------------------------------|-------------------------------------------|----------------------------------------------|----------------------------------------------|---------------------------|
|            | C <sub>Ag</sub><br>(mol.dm <sup>-3</sup> )  | C <sub>L</sub><br>(mol.dm <sup>-3</sup> ) |                                              |                                              |                           |
| EN         | 8.4x10 <sup>-6</sup> - 4.3x10 <sup>-2</sup> | 10 <sup>-3</sup> - 10 <sup>-1</sup>       | 9.8x10 <sup>-11</sup> - 1.1x10 <sup>-6</sup> | AgL <sub>2</sub> <sup>+</sup>                | 7.47±0.01                 |
|            |                                             |                                           |                                              | Ag <sub>2</sub> L <sub>2</sub> <sup>2+</sup> | 12.98±0.01                |
|            |                                             |                                           |                                              | Ag <sub>2</sub> L <sub>3</sub> <sup>2+</sup> | 14.54±0.02                |
| DIEN       | 7.6x10 <sup>-6</sup> - 2.1x10 <sup>-2</sup> | 10 <sup>-3</sup> - 10 <sup>-1</sup>       | 9.5x10 <sup>-11</sup> - 3.1x10 <sup>-6</sup> | AgL <sub>2</sub> <sup>+</sup>                | 7.84±0.01                 |
|            |                                             |                                           |                                              | Ag <sub>2</sub> L <sub>2</sub> <sup>2+</sup> | 14.71±0.01                |
|            |                                             |                                           |                                              | Ag <sub>2</sub> L <sub>3</sub> <sup>2+</sup> | 15.70±0.02                |
| GLY        | 1.3x10 <sup>-5</sup> - 3.1x10 <sup>-2</sup> | 10 <sup>-3</sup> - 10 <sup>-1</sup>       | 6.9x10 <sup>-10</sup> - 1.7x10 <sup>-6</sup> | AgL <sub>2</sub> <sup>-</sup>                | 6.75±0.01                 |
| IDA        | 6.5x10 <sup>-6</sup> - 1.0x10 <sup>-2</sup> | 10 <sup>-3</sup> - 10 <sup>-1</sup>       | 9.8x10 <sup>-9</sup> - 2.2x10 <sup>-6</sup>  | AgL <sub>2</sub> <sup>3-</sup>               | 5.72±0.01                 |
| NTA        | 1.6x10 <sup>-5</sup> - 7.2x10 <sup>-3</sup> | 10 <sup>-3</sup> - 10 <sup>-1</sup>       | 1.2x10 <sup>-8</sup> - 1.7x10 <sup>-6</sup>  | AgL <sub>2</sub> <sup>2-</sup>               | 4.70±0.01                 |

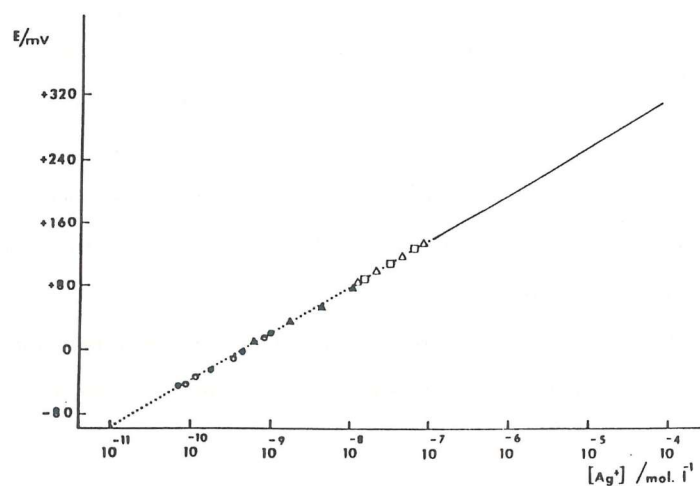


Fig. 1 - Potential response of a silver sulphide membrane electrode vs. free silver concentration. solid line - working curve in the absence of the ligands; dotted line - readings in the presence of the ligands (○ - ethylenediamine; ● - diethylenetriamine; ▲ - glycine; △ - imino-diacetic acid; □ - nitrilotriacetic acid).

species and a better precision of the stability constants than the calculations through pH variation.

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## WATER DETERMINATION IN ORGANIC SOLVENTS BY OSCILLOMETRY

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#### INTRODUCTION

The most common contaminant of organic solvents is water which is currently removed by drying and fractional distillation. The need for analysis of water content as a purity control of solvents or as a measure of the efficiency of purification treatments is a routine procedure in many areas of a chemical laboratory.

The widely used technique for quantitative water determination is the Karl Fischer titration, which requires special care with reagents and operation in order to obtain rigorous results. Several other methods are available, among them those based on dielectric properties which can be carried out in safer conditions of water contamination than titrations<sup>1</sup>.

In this paper results for the analysis of traces of water in organic solvents by oscillometry are presented. The method consists in measuring the change of capacitance of a liquid owing to the presence of water. As the dielectric constant of water is high, methods based on this property have good sensitivity in determining this compound in organic solvents, especially for those of low dielectric constant.