na figura 4. Observa-se a presença de um mínimo para x=0.10. A presença deste mínimo torna-se mais evidente após as 17 horas de evolução.

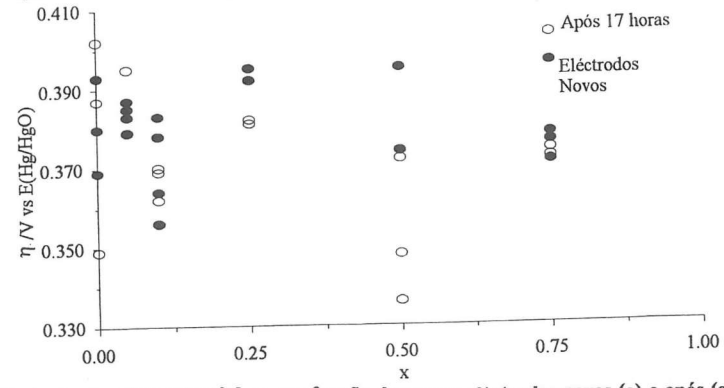


**Fig.4- Variação do sobrepotencial, η, em função de x para eléctrodos novos (•) e após (o) 17 horas sob evolução.**

**4. Conclusões :** O estudo da actividade electrocatalítica do sistema $Ni_{1-x}Cu_xCo_2O_4$ ($0.00 \leq x \leq 0.75$) relativamente à reacção de evolução do oxigénio, mostra que a presença do cobre não afecta os valores dos declives de Tafel. Contudo, observa-se uma diminuição do sobrepotencial e da densidade de corrente de troca com a introdução do cobre para valores até 10%. O estudo da actividade após 17 horas sob evolução, mostrou que os eléctrodos contendo cobre não apresentam modificações significativas nos valores de η, $I_0$ e b (baixo sobrepotencial). Pelo contrário, para os eléctrodos da espinela $NiCo_2O_4$ (x=0.00), após evolução prolongada de oxigénio, observa-se um aumento dos três parâmetros. Estes resultados apontam para um aumento da estabilidade dos eléctrodos com a intodução de cobre.

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# POTENTIOMETRIC MEASUREMENTS OF $K^+$ IN THE PRESENCE OF DIFFERENT TYPES OF PROTEINS

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ABSTRACT
Potentiometric measurements have been performed, at 25 °C, in cells of the type:

| Reference electrode | $10^{-2}$ mol $dm^{-3}$ KCl + x g $dm^{-3}$ albumin ( 20 < x < 100) | K ( I.S.E.) (I) |
|---|---|---|

Albumins of different types, reference electrodes with hypertonic and isotonic electrolytes, different forms of the liquid junction and methologies of measurements were studied.
Recently reported calculations (1) were applied and confirm the influence of proteins on liquid junction potentials.

## INTRODUCTION

The use of ion-selective-electrodes in clinical chemistry as well as in other applied fields is firmly established. Recently more than 30 commercial clinical analysers using I.S.E.(2) were reported. However there still exist some drawbacks with their use and different commercial instruments produce different values for the same sample when calibrated by the manufacturer's recommended procedure. One of the reasons for the observed discrepancies is the protein contribution to the global cell potential. The present work is part of a continuous effort to clarify the influence of protein in the liquid junction potential which is the "most poorly understood and the most variable feature among commercial analysers"(3)

## MATERIALS AND METHODS

Potassium chloride - Merck, proanalysis;Valinomycin - Sigma VO627; 2-Nitrophenyloctyl ether - Fluka, Selectophore; PVC - Fluka, pure; Potassium Tetrakys (4-chlorophenylborate) - Fluka, Selectophore; Tetrahydrophuran - Sigma T5267; Albumin - chicken egg Grade V, Sigma; Bovine serum albumin A3350 Sigma.

The solutions were prepared with conductivity water redistilled from distilled water, to which potassium permanganate and sodium hydroxide were added, under a current of nitrogen.

## ELECTRODES

Reference electrodes used were
*Hypertonic* - Commercial Saturated Calomel Electrode (◆,◊)
*Isotonic* - Substituted Calomel Electrode (inner solution KCl 0,15 mol $dm^{-3}$) with ceramic plug (●,○) and Ag/AgCl Electrode with dialysis membrane (■,□).

Valynomicin based potassium ion-selective electrodes were prepared in this laboratory.

## METHODOLOGY

Measurements were performed following two procedures for the variation of albumin (Bovine Serum Albumin (BSA) and Chicken Egg Albumin (CEA)) concentration

a) Dilution of an initial concentrated solution ( 100 g dm$^{-3}$ albumin in $10^{-2}$ mol dm$^{-3}$ KCl ) by addition of $10^{-2}$ mol dm$^{-3}$ KCl ( ◆,●,■). Fig.1,2 and Table 1.

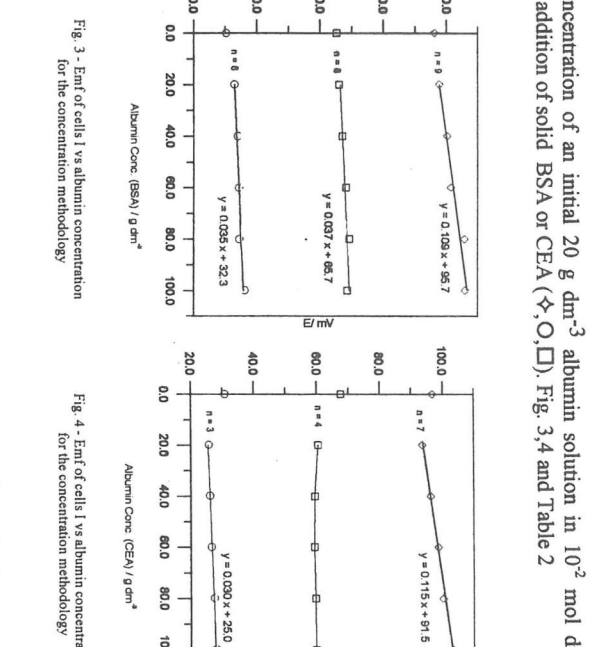


Fig.1 - Emf of cells I vs albumin concentration for the dilution methodology

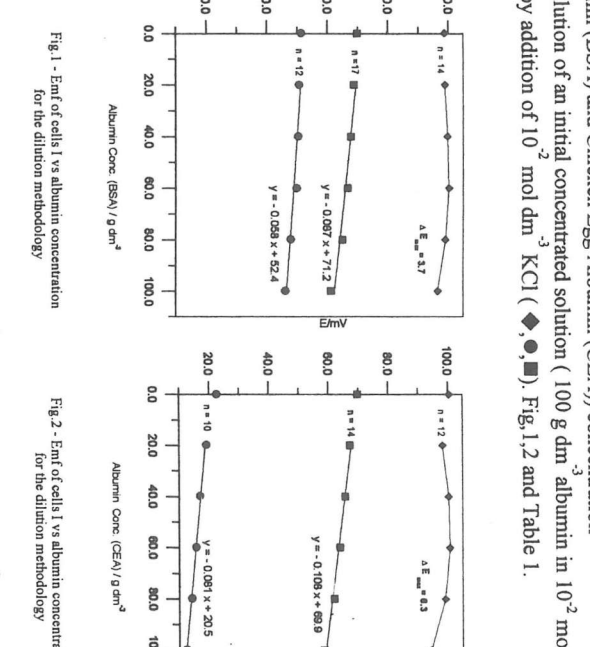


Fig.2 - Emf of cells I vs albumin concentration for the dilution methodology

b)Concentration of an initial 20 g dm$^{-3}$ albumin solution in $10^{-2}$ mol dm$^{-3}$ KCl by addition of solid BSA or CEA (✧,○,□). Fig. 3,4 and Table 2

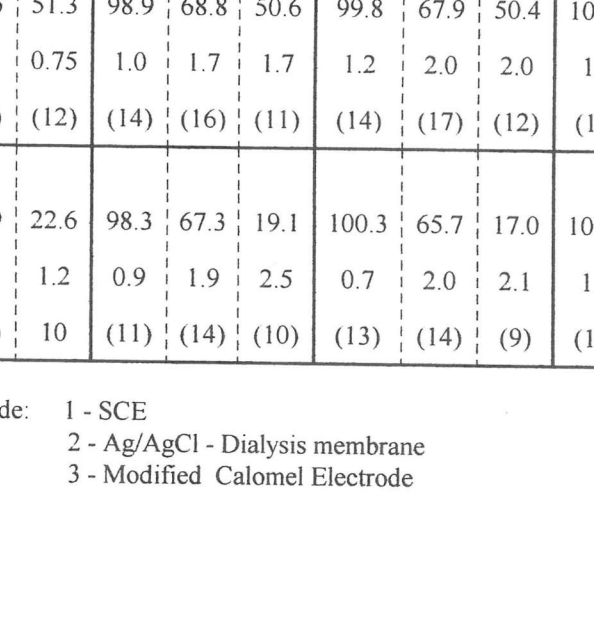


Fig. 3 - Emf of cells I vs albumin concentration for the concentration methodology

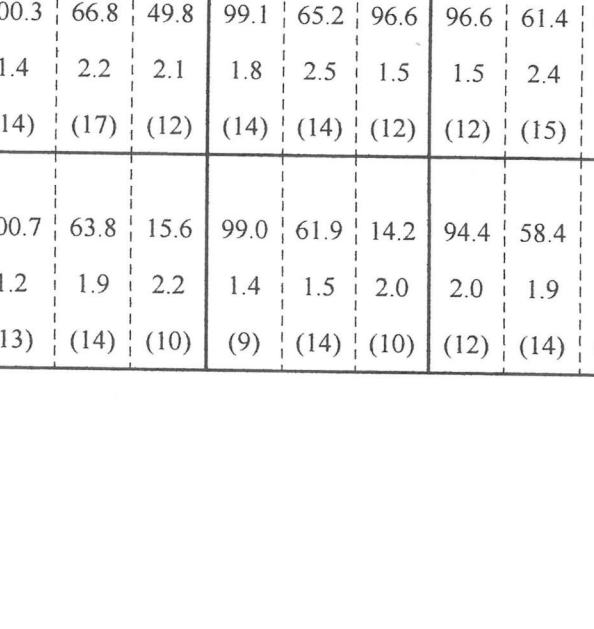


Fig. 4 - Emf of cells I vs albumin concentration for the concentration methodology

Subtracting the differences between emf of cell I when an isotonic and a hypertonic reference electrode are used in a solution with added albumin from a similar difference for a solution without albumin as described in (1) , residual liquid junction potentials shown in Table 3 were obtained. These results confirm the influence of albumin on the liquid junction potential.

Table 1 - Emf of cells I for the ***dilution*** methodology

| | Albumin Concentration / g dm$^{-3}$ | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | | | 20 | | | 40 | | | 60 | | | 80 | | | 100 | | |
| **BSA** | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| Emf. | 98.8 | 69.6 | 51.3 | 98.9 | 68.8 | 50.6 | 99.8 | 67.9 | 50.4 | 100.3 | 66.8 | 49.8 | 99.1 | 65.2 | 96.6 | 96.6 | 61.4 | 46.1 |
| SD | 0.9 | 1.5 | 0.75 | 1.0 | 1.7 | 1.7 | 1.2 | 2.0 | 2.0 | 1.4 | 2.2 | 2.1 | 1.8 | 2.5 | 1.5 | 1.5 | 2.4 | 2.3 |
| n | (12) | (17) | (12) | (14) | (16) | (11) | (14) | (17) | (12) | (14) | (17) | (12) | (14) | (14) | (12) | (12) | (15) | (9) |
| **CEA** | | | | | | | | | | | | | | | | | | |
| Emf | 1005 | 69.9 | 22.6 | 98.3 | 67.3 | 19.1 | 100.3 | 65.7 | 17.0 | 100.7 | 63.8 | 15.6 | 99.0 | 61.9 | 14.2 | 94.4 | 58.4 | 12.4 |
| SD | 2.0 | 1.1 | 1.2 | 0.9 | 1.9 | 2.5 | 0.7 | 2.0 | 2.1 | 1.2 | 1.9 | 2.2 | 1.4 | 1.5 | 2.0 | 2.0 | 1.9 | 1.9 |
| n | (9) | (11) | 10 | (11) | (14) | (10) | (13) | (14) | (9) | (13) | (14) | (10) | (9) | (14) | (10) | (12) | (14) | (10) |

Ref. electrode: 1 - SCE
2 - Ag/AgCl - Dialysis membrane
3 - Modified Calomel Electrode

Table 2 - Emf of cells I for the ***concentration*** methodology

Albumin Concentration / g $dm^{-3}$

| | 0 | | | 20 | | | 40 | | | 60 | | | 80 | | | 100 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BSA | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| Emf. | 96.4 | 65.3 | 30.3 | 96.8 | 66.1 | 32.9 | 100.3 | 67.1 | 33.9 | 102.2 | 68.3 | 34.4 | 105.8 | 69.3 | 34.5 | 105.5 | 68.7 | 36.1 |
| SD | 1.4 | 2.0 | 1.7 | 1.8 | 1.0 | 1.0 | 1.7 | 1.8 | 1.8 | 1.7 | 1.9 | 1.3 | 2.0 | 2.9 | 1.4 | 2.2 | 2.7 | 1.1 |
| n | (9) | (7) | (5) | (7) | (5) | (4) | (11) | (8) | (6) | (11) | (8) | (6) | (6) | (5) | (3) | (9) | (8) | (6) |
| CEA | | | | | | | | | | | | | | | | | | |
| Emf | 96.9 | 67.8 | 30.9 | 93.7 | 60.4 | 25.8 | 96.3 | 59.5 | 26.0 | 98.6 | 59.4 | 26.6 | 100.2 | 59.6 | 27.5 | 103.3 | 60.0 | 28.0 |
| SD | 1.1 | 0.4 | 0.5 | 1.1 | 0.4 | 0.9 | 1.0 | 0.3 | 0.4 | 1.4 | 1.3 | 0.1 | 1.3 | 0.8 | 0.1 | 2.2 | 0.4 | 0.4 |
| n | (7) | (4) | (3) | (7) | (4) | (3) | (7) | (4) | (3) | (7) | (4) | (3) | (7) | (4) | (3) | (7) | (4) | (5) |

Ref. electrode: 1 - SCE
2 - Ag/AgCl - Dialysis membrane
3 - Modified Calomel Electrode



Table 3. Residual Liquid Junction Potential

| | Dilution Methodology ($E_{Mod\ CE,0} - E_{SCE,0}$) i | | | | | Concentration Methodology ($E_{ModCE,i} - E_{SCE,i}$) i | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 20 | 40 | 60 | 80 | 100 | 20 | 40 | 60 | 80 | 100 |
| BSA | 0,8 | 1,9 | 3,0 | 5,0 | 3,5 | -2,2 | 0,3 | 1,7 | 5,2 | 3,3 |
| CEA | 1,3 | 5,4 | 7,2 | 6,9 | 4,1 | 1,9 | 4,3 | 6,0 | 6,7 | 9,3 |

($E_{Iso,AgCl,0} - E_{SCE,0}$) - ($E_{Iso,AgCl,i} - E_{SCE,i}$)

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| BSA | 0,9 | 2,7 | 4,3 | 4,7 | 6,0 | -0,4 | 2,1 | 2,8 | 5,4 | 5,7 |
| CEA | 0,4 | 4,0 | 6,3 | 6,5 | 5,4 | 4,2 | 7,7 | 10,1 | 11,5 | 14,2 |

Mod CE - modified calomel electrode (Isotonic)
Iso AgCl - isotonic silver/silver chloride electrode

DISCUSSION AND CONCLUSIONS

It is observed that there is a negative correlation of emf values with albumin concentration when the dilution methodology is used for both albumin types and isotonic reference electrodes. The variation is slightly curvilinear when SCE is used.
Moreover the variation when isotonic reference electrodes are used is larger than when SCE is.
On the other hand there is a general tendency for a positive correlation of emf values with albumin concentration when the concentration methodology is used, the variation being larger when SCE is used than with isotonic reference electrodes are.
It is confirmed that albumin influences the liquid junction potential.

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