

## STUDIES WITH A SODIUM ION SELECTIVE ELECTRODE USING A CALIX[4]RENE AS IONOPHORE

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### Abstract

A PVC membrane containing the tetra ethyl ester of p-tert-butyl calix[4]arene as ionophore was prepared and tested for sodium ion in solutions with and without albumin (BSA), after confirmative experiments with respect to Nernstian behaviour, limit of detection, selectivity to  $K^+$ , reproducibility and lifetime.

Measurements of  $Na^+$  have been taken in solutions of albumin containing constant  $0.01 \text{ mol dm}^{-3}$  NaCl solution. The protein concentration ranged from 0 to  $100 \text{ g dm}^{-3}$  in increments of  $20 \text{ g dm}^{-3}$ .

The reference electrodes were of two types, hypertonic (saturated calomel electrode) and isotonic (Ag, AgCl,  $0.15 \text{ mol dm}^{-3}$  KCl). Variation of potential with albumin concentration is larger than expected [2] and bigger for hypertonic than for isotonic reference electrodes. Explanation was found in the presence of sodium contamination of the protein.

**Keywords:** Ion selective electrodes; Protein effect; Isotonic and hypertonic electrolytes in reference electrodes.

### Introduction

Calixarenes, macrocyclic compounds produced by the condensation of p-alkyl phenols with formaldehyde are an interesting class of molecules since they are easily synthesised, being also excellent complexing agents [1].

After decades of research on ISE, expectation has been put on calixarenes [3]. Successful use as sodium ion selective electrodes is well documented [3,4].

The use of ion selective electrodes in clinical chemistry is well recognised. However, some discrepancies are observed between the different commercial instruments available. The protein influence in the measurements and particularly in the liquid junction potential was studied for different reference electrode solutions, hypertonic (saturated KCl) and isotonic ( $0.15 \text{ mol dm}^{-3}$  KCl).

### Experimental

#### Chemicals

Sodium chloride - Merck, proanalysis; Potassium chloride - Merck, proanalysis; 2-nitrophenyl octyl ether (*o*-NPOE) - Fluka, Selectophore; PVC - Fluka, Selectophore; Potassium tetrakis(4-chlorophenyl)borate (KTPCIPB) - Fluka, Selectophore; Tetrahydrofuran - Sigma T5267; Bovine serum albumin (BSA) - Sigma A3425. The calixarene was synthesised by another research group of the Department.

The solutions were prepared by dilution of BSA in  $0.01 \text{ mol dm}^{-3}$  NaCl solution.

Conductivity water redistilled from distilled water with added potassium permanganate and sodium hydroxide under a current of nitrogen was used to prepare the solutions.

#### Electrodes / Methodology

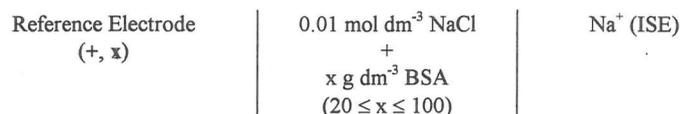
- Reference electrodes were:

Hypertonic - Commercial saturated calomel electrode (SCE) Metrohm 60701.100 (+).

Isotonic - Thermoanalytical [5] Ag, AgCl, 0.15 mol dm<sup>-3</sup> KCl contained in a polycarbonate tube to which a dialysis membrane was fitted (x).

- Ion selective electrodes (Na<sup>+</sup>(ISE)): - Polycarbonate tubes with a ethyl ester of p-tert-butyl calix[4]arene based membrane (ionophore - 5 mg, PVC - 167,5 mg, o-NPOE - 330 mg, KTpCIPB - 50 mol % wrt ionophore) fitted by means of o-rings containing an Ag, AgCl inner reference electrode, in 0.1 mol dm<sup>-3</sup> NaCl.

Potentiometric measurements have been performed, at 25.0 °C (water-thermostated bath), in cells of the type:

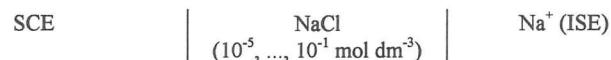


with a HP 3421A data acquisition/control unit interfaced with a HP-85 computer. Measurements were made in increasingly diluted and increasingly concentrated albumin solution.

### Results and Discussion

#### Calibration of the Electrodes

Calibration of the electrodes was done measuring the cells of the type:



Values were recorded for three ISE's and the corresponding calibration graphs are shown in figure 1.

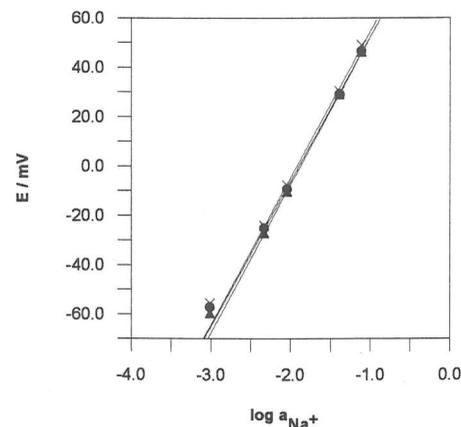


Figure 1 - Calibration graph for ion selective electrodes A(+), B(x) and C(▲).

The results revealed a Nernstian response to sodium ions. The response characteristics of ISE are summarised in Table 1.

Table 1 - Response characteristics of the sodium selective electrode

Parameter	ISE
Slope / mV decade <sup>-1</sup>	59.36
Standard deviation / mV decade <sup>-1</sup>	0.63
Correlation coefficient	0.999
Linear range / mol dm <sup>-3</sup>	5.10 <sup>-4</sup> - 0.1
Detection limit / mol dm <sup>-3</sup>	6.9.10 <sup>-5</sup>

#### Selectivity coefficient

The selectivity coefficient ( $k_{Na-K}^{pot}$ ) was calculated using the fixed interference method [6]. The response curves obtained experimentally with four ISE's are shown in figure 2. The mean selectivity coefficient and standard deviation obtained are 2.8.10<sup>-2</sup> and 4.3.10<sup>-3</sup>, respectively. The obtained value is similar to the one reported in [7].

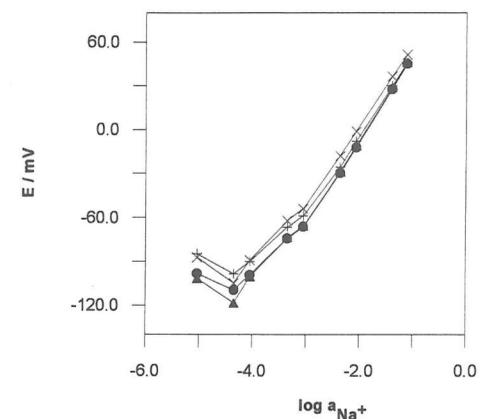


Figure 2 - Experimental curves obtained with ISE's A to D, in solutions containing constant 0.01 mol dm<sup>-3</sup> KCl and variable concentration of NaCl.

#### Lifetime Studies

The ISE's were repeatedly calibrated during a period of 8 weeks. No change in the performance of the electrode was observed for 6 weeks. The slope of the calibration graph deteriorated to 58.52 mV after the 7th week and to 50.47 mV after the 8th week.

#### Study of the behaviour of the Na<sup>+</sup> selective electrode in the presence of protein

To clarify the protein effect the sodium ion selective electrodes were used in sodium chloride solutions containing albumin vs isotonic and hypertonic KCl reference electrodes. Measurements

were made on BSA solutions after several days of preparation (1-6), figure 3. The sequence of measurements was done in increasingly concentrated albumine solution, figura 4 a) and on increasingly diluted albumin solution, figura 4 b). The results of both series are comparable.

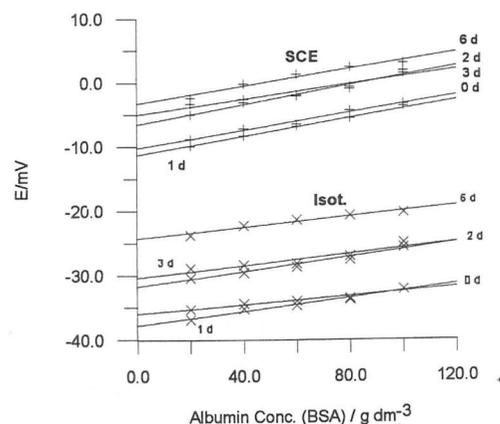


Figure 3 - Study of the behaviour of the electrodes with the lifetime of BSA solutions.

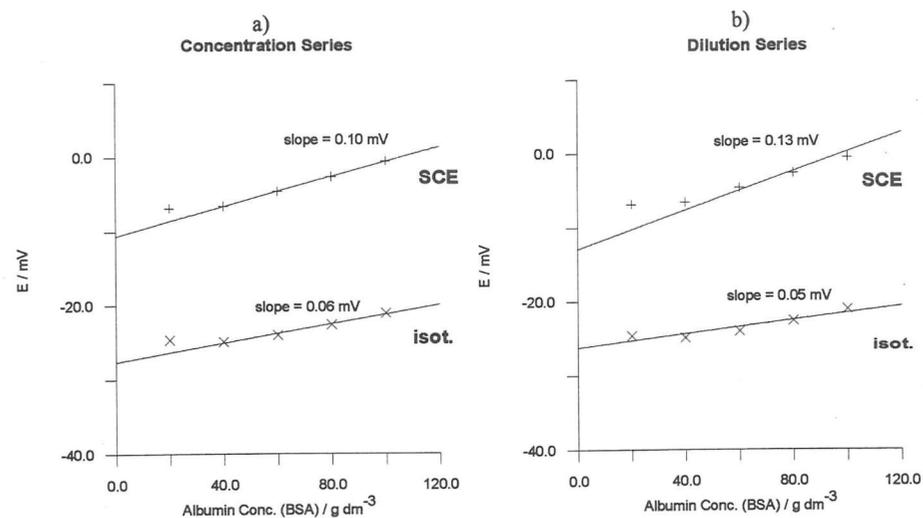


Figure 4 - Study of the behaviour of the electrodes in concentration and dilution series.

It was observed that both slopes were positive, being bigger for hypertonic than for isotonic reference electrodes. The age of BSA solutions has no significant influence on the trend of results.

These observations were unexpected, when compared with potassium selective electrodes in albumin containing solutions [2,8,9]. Explanation was found in the presence of sodium contamination of the protein, which was confirmed by AA spectroscopy.

A sodium concentration of  $1.1 \cdot 10^{-4}$  mol  $\text{dm}^{-3}$  was found in a solution of 20  $\text{g dm}^{-3}$  BSA in water. Evidence of the albumin influence on the liquid junction potential is shown in the results obtained by subtraction of the appropriate differences between e.m.f. of cells containing albumin solutions from those without albumin, Table 2.

Table 2 - Subtraction of the appropriate differences between e.m.f. (mV) of cells with [i ( $\text{g dm}^{-3}$ )] albumin and without (i=0) albumin.

i = BSA $\text{g dm}^{-3}$	$(E_{\text{SCE},0} - E_{\text{Ag/AgCl},0}) - (E_{\text{SCE},i} - E_{\text{Ag/AgCl},i})$
20	-1.7
40	-2.4
60	-3.3
80	-3.6
100	-4.4

According to the Henderson equation, the presence of sodium in the BSA sample also explains the differences between the measurements with the two reference electrodes.

### Conclusions

Sodium ion selective electrodes using tetra ethyl ester of p-tert-butyl calix[4]arene as the ionophore prepared by us, show Nernstian behaviour and selectivity to  $\text{K}^+$  that enable  $\text{Na}^+$  measurements without significant interference.

Studies of the albumin influence on ISE response were done with these electrodes. The increase of the e.m.f. response with albumin concentration (BSA) in NaCl containing solutions was found to be mainly due to the sodium content of BSA sample used. These latter observation was checked by atomic absorption spectroscopy. Different slopes observed for different reference electrodes evidence, once more, the importance of the liquid junction contribution to the overall cell potential.

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