

Final Comments

The redox properties of the zero valent complexes $[\{ML_2\}_2(\mu-P^{\wedge}P)_2]$ ($M=Ni$ or Pd ; $P^{\wedge}P=PPh_2CH_2C(Bu^t)=N-N=C(Bu^t)CH_2PPh_2$) are dependent on their composition, in particular on the transition metal, e.g., no palladium oxidation was detected in contrast with nickel complexes.

The reductive electron transfer to the palladium dimer $[\{Pd(MeCO_2C\equiv CCO_2Me)\}_2(\mu-P^{\wedge}P)_2]$ induced chemical reactivity and alkyne to vinyl and azine to ene-hydrazone conversions occurred, in addition to palladium-phosphorus bond breaking, as well as Pd-P and Pd-N bond formation, affording $[Pd(PPh_2CH_2C(Bu^t)=N-N-C(Bu^t)=C(H)PPh_2)(MeCO_2C=C(H)CO_2Me)]$.

Acknowledgments

This work was partially supported by Junta Nacional de Investigação Científica e Tecnológica (JNICT), the PRAXIS XXI program, Fundação Caloust Gulbenkian (Portugal) and the grant N° 203/97/1157 from the Grant Agency of the Czech Republic.

References

- [1] S.D. Perera, B.L. Shaw, M. Thornton-Pett, *J.Chem.Soc., Dalton Trans.* (1992) 1469.
- [2] S.D. Perera, B.L. Shaw, M. Thornton-Pett, *J.Chem.Soc., Dalton Trans.* (1993) 3653.
- [3] J. Čermák, Šabata, paper in preparation.
- [4] M.F.N.N. Carvalho, J. Čermák, A.J.L. Pombeiro, S. Šabata, paper in preparation.

POTENTIOMETRIC STUDIES WITH BIOCOMPATIBLE POLYURETHANE- BASED MEMBRANES

Gomes, Ana M.R.*; Oliveira, Cristina M.R.R.*; Rebelo, M.J.F.*; Camões, M.F.G.F.C.*

* CECUL - Centro de Electroquímica e Cinética da Universidade de Lisboa.

*-Departamento de Química e Bioquímica da Faculdade de Ciências de Lisboa.
Rua da Escola Politécnica N° 58 1294 LISBOA CODEX

ABSTRACT

Polyurethane has been used lately as an alternative to PVC in the preparation of ISE membranes for clinical applications. This is due both to its biocompatibility [1] and to the claimed elimination of the protein asymmetry effect produced by serum at conventional PVC membranes [2].

Following previous work [3-7] electrodes have been prepared with TECOFLEX SG - 80A polyurethane and K^+ measurements have been performed in Bovine Serum Albumin (BSA) containing solutions.

Effects such as albumin concentration, sequence and age of solutions have been tested.

Simultaneous readings, in the same solution, have been taken with PVC based membranes and with polyurethane based ones vs. Saturated Calomel Electrode (SCE) and isotonic KCl electrodes (Ag/AgCl and Modified CE)

The results follow similar trends, without significant distinction being observed.

Therefore, the effects of protein on the potentiometric measurements, due to interaction with the membrane, if any, seem to be independent of the polymers tested.

These observations add evidence to the importance of the liquid-liquid junction potential contribution to the overall measurements.

Key Words - PVC, Polyurethane, membranes, K^+ selective electrode.

INTRODUCTION

Ion-selective electrodes are routinely used in clinical chemistry as well as in other applied fields despite the fact that some factors affecting the accuracy of measurements are still to be clarified [7].

This work follows previous studies [3-7] dealing with the influence of albumin and of reference electrode characteristics to the global cell potential. At this time we were interested in testing whether any difference is observed when the composition of the sensor membrane is modified from PVC to PU or not. In fact, this latter material has been lately used more as an alternative to PVC due to its characteristics concerning biocompatibility [1] and the elimination of the protein asymmetry effect produced by serum at conventional PVC membranes [2].

MATERIALS AND METHODS

KCl - Merck, P.A.; Valinomycin - Sigma V-0627; 2-Nitrophenyloctylether - Fluka, Selectophore; PVC - Fluka, pure; Polyurethane (PU) - "Tecoflex" SG-80A, Thermedics, Inc.; Potassium Tetrakis (4-chlorophenylborate) - Fluka, Selectophore; Tetrahydrofuran - Sigma T-5267; Bovine Serum Albumin (BSA) - Sigma A-3350

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- SCE, Metrohm 60701.100 - *

Isotonic → Modified Calomel Electrode (0.15 mol dm⁻³ KCl was substituted for manufacturer's inner saturated KCl solution) with a ceramic plug - Mod. CE. - ■

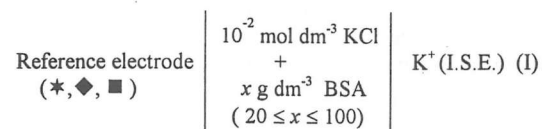
→ Silver-Silver Chloride Electrodes - Ag/AgCl - prepared by the thermoelectrolytic method in our laboratory [8] as suggested by Bates [9]. They were either used as an external (dipped in a 0.15 mol dm⁻³ KCl solution contained in a polycarbonate tube whose ending has an 1mm diameter orifice; to this ending a dialysis membrane is applied with an O-ring) (◆) or as an internal reference electrode for the K⁺SE (dipped in a 10⁻² mol dm⁻³ KCl solution).

Selective electrodes:

Valinomycin based potassium ion-selective electrodes were prepared in this laboratory: 5 mg of valinomycin, 167.5 mg PVC or PU, 330 mg of o-NPOE and 50% (mole % ionophore) of potassium tetrakis were dissolved in freshly distilled, under N₂, THF. The mixture was stirred overnight, put on a PTFE mould and allowed to dry. Several discs were cut from the same preparation and each one was applied to a polycarbonate stem with an O-ring. 10⁻² mol dm⁻³ KCl solution and Ag/AgCl inner reference electrode were introduced in the stem.

METHODOLOGY

Potentiometric measurements were performed in cells of the type:



*- SCE ◆- Ag/AgCl (Isotonic KCl) ■- Mod. CE (Isotonic KCl)

with a Hewlett Packard data acquisition/control unit, HP 3421A, interfaced with a HP-85 computer, in a water thermostated bath, at 25.0°C.

Measurements were taken in increasingly diluted (**dilution sequence**) and increasingly concentrated (**concentration sequence**) albumin - Bovine Serum Albumin (BSA) solutions.

Each albumin concentration solution (20, 40, 60, 80 g dm⁻³) was prepared from direct dilution of a 100 g dm⁻³ stock solution with 10⁻² mol dm⁻³ KCl. [5]. The solutions were stored in the refrigerator at $\approx 5^\circ\text{C}$ between experimental runs.

RESULTS AND DISCUSSION

The trends shown by values of potential for K⁺ ISE vs. albumin containing solutions are similar for PU and PVC ones when comparing results for albumin dilution sequence. The same can be said for concentration sequence, although results for concentration sequence and for dilution show some different features. Figs.1 a) and b).

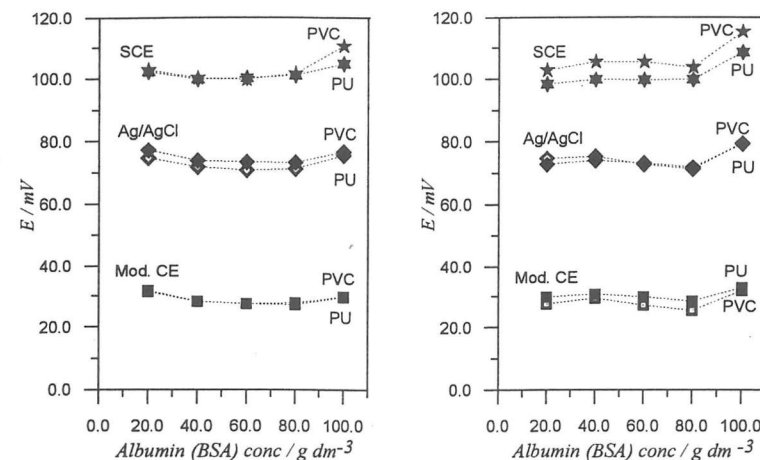


Fig.1-a) -Emf measurements with PU and PVC K⁺ electrodes. Average values (1st- nth day) Dilution sequence

Fig.1-b) -Emf measurements with PU and PVC K⁺ electrodes. Average values (2nd- nth day) Concentration sequence

Average measurements for each of 4 consecutive days show a consistent increase for the most concentrated albumin solutions when compared with values for lower albumin concentrations. This systematic increase, evidenced by a detailed analysis of the results day after day, proves the existence of an ageing effect on the protein solutions, Fig.2., which has already been reported [7] for HSA containing solutions.

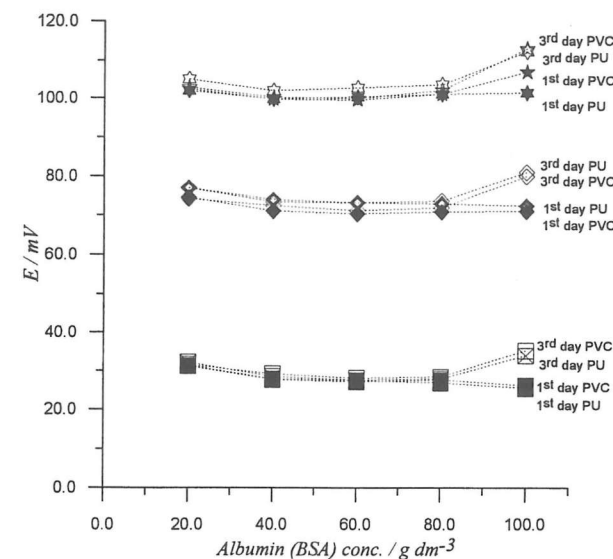


Fig.2 - Emf measurements with PU and PVC K⁺ electrodes at 1st and 3rd day. Dilution sequence

Similarity of features for PVC based electrodes and PU based ones is confirmed, therefore, the effect of protein on the potentiometric measurements, due to interaction with the membrane, seem to be independent of the polymers tested. Comparison of results was done for 1st day measurements, Fig.3.

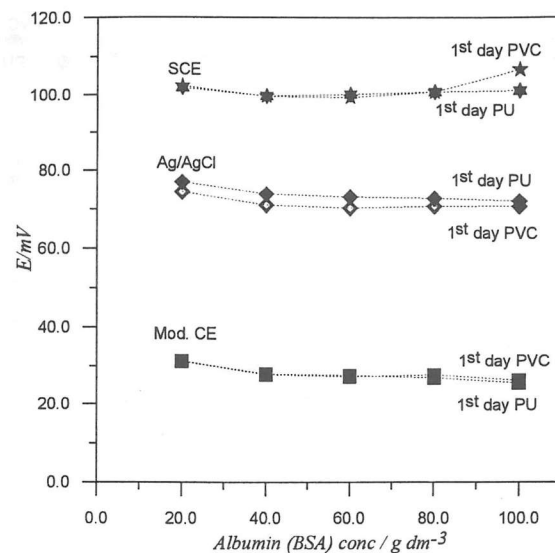


Fig.3 - Emf measurements with PU and PVC based K⁺ electrodes

For a better fitting, linear regression was done for the concentration range 40 to 100 g dm⁻³ albumin. The slopes of emf vs. albumin concentration are negative for isotonic junctions and positive for hypertonic ones. Table 1.

Table 1 - Average slopes (mV/g dm⁻³) and the corresponding standard deviations for the variation of emf vs albumin concentration of the different studied membranes.

Membrane		PU	PVC
Ref. Electrode			
SCE (Hypertonic)	slope	0.026	0.112
	SD	0.0021	0.049
Ag / AgCl (Isotonic)	slope	-0.028	-0.0010
	SD	0.0019	0.0093
Mod. CE (Isotonic)	slope	-0.041	-0.021
	SD	0.065	0.012

This observation adds evidence, to the importance of the liquid-liquid junction potential contribution to the overall measurements.

REFERENCES

1. Cha, G.S.; Liu, D.; Meyerhoff, M.E., *et al.*, *Anal. Chem.* **63**, 1666-72 (1991).
2. D'Orazio, P.; Laios, I.; Bowers Jr., G.N., 14th International Symposium of AACC-Electrolyte/Blood Gas Division. Chatham (1992).
3. Rebelo, M.J.F., *Port. Elect. Acta*, **13** (1995) 79-94
4. Oliveira, C.M.R.R.; Rebelo, M.J.F.; Camões, M.F.G.F.C., *Port. Elect. Acta*, **13**, (1995) 461-465
5. Oliveira, C.M.R.R.; Rebelo, M.J.F.; Camões, M.F.G.F.C., *Analyst*, **121**, (1996) 1907-10
6. Oliveira, C.M.R.R.; Rebelo, M.J.F.; Camões, M.F.G.F.C., *In: D'Orazio P. ed. "Preparing for Critical Care Analysis in the 21st Century*, 282-95, 1996.
7. Oliveira, C.M.R.R.; Rebelo, M.J.F.; Camões, M.F.G.F.C., *Port. Elect. Acta*, **14** (1996).217-221
8. Oliveira, C.M.R.R., MSc. Thesis, Fac. of Sciences, University of Lisbon, 1992.
9. Bates, R.G., "Determination of pH", Wiley, New York, 2nd ed., 1973.