GLASS TRANSITION TEMPERATURES OF POLY(VINYL CHLORIDE) AND POLY(ACRYLATE) MATERIALS AND CALCIUM ION-SELECTIVE ELECTRODE PROPERTIES[a]

G.J.Moody, B.Saad and J.D.R.Thomas
Department of Applied Chemistry, Redwood Building,
UWIST, PO Box 13, Cardiff CF1 3XF.

INTRODUCTION

Poly(vinyl chloride) (PVC) is the most commonly used polymer support for fabricating ISEs with diverse sensor cocktails.[1,2] Considerable research effort has been expended on the rôles of the sensor and the mediator in such cocktails. However, relatively little information is available on the PVC matrix except for occasional reference to its molecular mass and the almost 30% mass content needed to realise sensor membranes with suitable mechanical strength.

Alternative polymer matrices, such as poly(methyl acrylate)[3], poly(vinyl 2-methyl propyl ether)[4], Urushi[5], and a block copolymer of poly(bisphenol-A carbonate) and poly(dimethylsiloxane)[6] and polyurethane[7] are also suitable but none seriously challenge the established popularity of PVC. This relates partly to its high tensile strength, easy fabrication and glass transition temperature T_g.

The well-known reduction in the T_g values of polymers by plasticising solvents has not been seriously studied in relation to the performance of PVC ISEs. This paper concerns an evaluation of calcium ISEs based on a cocktail of calcium bis{di-[4-(1,1,3,3-tetramethyl butyl)phenyl]-phosphate}, CaX_2, and several different solvent mediators when incorporated in nine different PVCs, a poly(methyl acrylate), three poly(methacrylates) and also the measurement of T_gs, alone, and with incorporated calcium sensor cocktails[8].

EXPERIMENTAL

All ISEs were fabricated and evaluated in the usual manner[1] and T_g measurements were undertaken by differential scanning calorimetry (DSC) for polymers alone and their master membranes containg various cocktails.

The Breon Resin III EP PVC ($\overline{M}_w$>100,000) was obtained from British Petroleum. The seven PVC samples with weight-average relative masses ($\overline{M}_w$) ranging from 81330 to 175300 were produced for the IUPAC Working Party on their fine structure and thermal stability (gifts from Dr.G.S.Park, UWIST). The ninth PVC sample ($\overline{M}_w$ = 70,000) was supplied by Aldrich.

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The poly(methyl acrylate) was prepared as described by Hassan et al.[3] Poly(methyl methacrylate) ($\bar{M}_w$ 90,000) was obtained from Aldrich. Poly(butyl methacrylate) and poly-(2-methylpropyl methacrylate) were obtained from Monomer-Polymer (Leominster, MA).

All solutions were prepared using doubly distilled de-ionised water and chlorides of the metals.

RESULTS AND DISCUSSION

The ISE incorporating PVC Breon III EP and CaX_2 with dioctylphenyl phosphonate (DOPP) constitutes the standard calcium ISE model in this study and where T_g value (-65°C) is less than that of the parent polymer alone (98°C) but near that of a membrane with no calcium salt (-67°C, Fig.1).

This large change in T_g values has also been observed for master membranes comprising Breon III EP with valinomycin/dioctyl adipate and nonactin/dioctyl adipate respectively.[9]

No important difference in terms of response times, selectivity coefficients, Nernstian slopes, membrane resistances or pH-emf profiles were exhibited by the nine PVC-based calcium electrodes when first fabricated or indeed 12 weeks later. It is interesting to note that Lakshminarayanaih[10] could not fabricate functional calcium ISEs from low molecular mass Aldrich PVC and the same CaX_2-DOPP cocktail employed in the present work (See Table 1). Thus it is imperative to employ a proven PVC, for example Breon 111 EP, Flowell 470 or Fluka S704 otherwise non-functional, or poor quality ISEs may be produced even with a well-established sensor cocktail.

The characteristics of PVC ISEs with a thicker sensor membrane cut from a master membrane ($\bar{t}$ = 0.87 mm, sd = 0.01, n = 10) comprising twice the standard quantitites of Breon III EP/CaX_2/DOPP were essentially identical with those mentioned above for the standard model where the mean membrane thickness $\bar{t}$ = 0.53 mm, sd = 0.03 (n = 10).

Functional calcium electrodes could also be fabricated with a poly(2-methyl propyl methacrylate) matrix but not with poly(butyl methacrylate), poly(methyl methacrylate) or poly(methyl acrylate) matrices. (Table 1).

Despite the fact that the T_g value for poly(2-methyl propyl methacrylate) (75°C) is similar to those (85°C to 102°C) measured for the nine PVCs, poly(methyl methacrylate), T_g = 108°C, gives a non-viable ISE membrane. Evidently properties other than just the T_g of polymers are associated with their electrochemical performance.

Fig.1 DSC Profiles of Various Polymer Master Membranes

PMA = Poly(methyl acrylate)

PMMA = Poly(methyl methacrylate)

P2MPMA = Poly(2-methylpropyl methacrylate)

DOPP = Dioctylphenyl phosphonate

TOP = Trioctylphosphate

TPP = Tripentylphosphate

CaX_2 = Calcium bis-{di[4-(1,1,3,3-tetramethyl butyl)phenyl] phosphate}

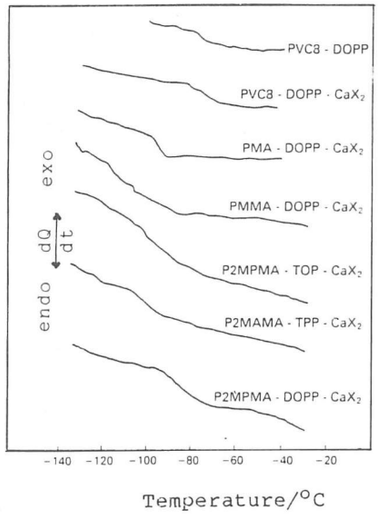

Table 1. Some Characteristics of Poly(2-methylpropyl methacrylate) and poly(vinyl chloride) calcium ISEs

Mediator	Slope /mV decade^{-1}	$k^{pot}_{Ca,B}$ [a] B=Mg	B=Na	B=K	Resistance /MΩ
Trioctyl phosphate	19.5	-	-	-	558
Tripentyl phosphate	26.3	7.4×10^{-3}	0.17	0.14	12
Dioctylphenyl phosphonate	27.4	8.4×10^{-3}	0.19	0.17	26
Standard Breon PVC IIIEP model	28.0	2.8×10^{-3}	9.7×10^{-2}	1.0×10^{-2}	3
Aldrich PVC[b] model	31.0	2.1×10^{-3}	8.1×10^{-2}	6.6×10^{-2}	1.4

[a] Separate solution method, [B] = 0.01M
[b] Low molecular mass

CONCLUSION

There were no important differences in terms of the parameters evaluated for the PVC electrodes assembled from the nine PVC materials. Nonetheless, the Breon IIIEP PVC will remain our first choice simply because it is readily available in large amounts. Even the best of the alternative acrylate polymers, namely poly(2-methylpropyl methacrylate), provides an inferior sensor matrix for the organophosphate-based liquid ion-exchanger calcium cocktail used.

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ADSORPTIVE STRIPPING VOLTAMMETRY: A VERSATILE TECHNIQUE FOR ENVIRONMENTAL AND CLINICAL STUDIES

Arnold G. Fogg and Ruth M. Fleming

Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire, UK

Electroactive organic compounds that adsorb strongly on mercury can be determined at very low concentrations by adsorptive stripping voltammetry at a hanging mercury drop electrode[1]. The compound is accumulated from a reproducibly stirred solution by adsorption at a newly-formed mercury drop for a suitable fixed time before being determined in quiescent solution by means of a potential sweep method. The technique is being used increasingly for the determination of drug compounds, and also for the determination of reducible metal ions after adsorption as chelate complexes[1].

The present increasing interest in adsorptive stripping voltammetry has been made possible by the introduction of modern static mercury drop electrode stands, such as the PAR 303 and the Metrohm 646 and 663, which allow virtually instantaneous automatic production and renewal of hanging mercury drop electrodes. The use of a microprocessor-controlled