Studies of difurylmethane–maleic anhydride copolymer as an ion-responsive membrane for the determination of mono-, di- and tri-valent cations

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SUMMARY: The synthesis of the difurylmethane-maleicanhydride(DFM-MAH) copolymer was done by reacting difurylmethane with maleic acid followed by hydrolysis with sodium hydroxide to produce the anhydride sodium salt. Construction of a sensor with the copolymer as the ion-exchanger material was done by mixing the copolymer with poly(vinylchloride), PVC, plastic matrix and dibutylphthalate (DBP) plasticizer in tetrahydrofuran (THF) solvent to form a paste. The paste was coated on a piece of silver wire to produce a coated wire electrode (CWE). The response characteristics of the copolymer-CWE, in potentiometric analysis, were studied for mono-, di- and tri-valent cations. All the cations studied showed a near-Nernstian response for concentrations ranging from 5×10^{-8} M to 1×10^{0}M in triethanolamine buffer in aqueous media (0.5 M, pH 10.5). The membrane had a composition of 20:20:60 for the copolymer, PVC and DBP.

Introduction

Since the construction of the first coated wire electrode (CWE) by Catrall *et al*$^{1)}$, numerous electrodes based on similar construction principle have been reported$^{2\text{-}14)}$. Most have reported on the fabrication of ion-selective electrodes (ISEs) that respond to either one ion or a couple of ions, usually containing similar charges. In this study, various cations carrying one, two and three charges were detectable, showing a near-Nernstian response for each ion. This universal response (non-specific) of an electrode to various cations was seen as an advantage because the electrode could be used as a detector for metal ions in ion chromatography. Usually the main disadvantage of coupling ISEs with the technique of ion chromatography is their high selectivity response to one or a limited number of ions. Nevertheless, the number of applications of potentiometric detection in ion chromatography is large. In 1993

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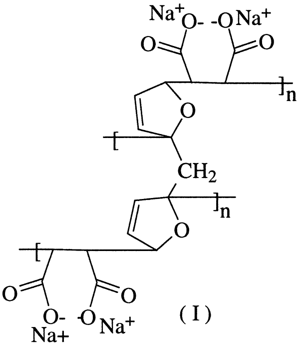
Isildak and Covington[15)] quoted 65 references that had been cited by 1992. In their work they reported on the use of anion- and cation-responsive, all solid-state, tubular PVC membrane electrodes as detectors in non-suppressed ion chromatography. However, their ISE detector was selective and sensitive to monovalent cations only, mainly to sodium and potassium and with no interference from other cations. The motivation to fabricate the coated wire electrode reported in this work was triggered by the synthesis in our lab[16)] of the difurylmethane-maleic anhydride cross-linked copolymer. Upon alkaline hydrolysis this copolymer forms an insoluble copolymer salt **(I)** that exhibits ion-exchange properties to cations. Other related furan-maleic anhydride polymers, in which the basic repeat unit is a furan-maleic anhydride moiety, were found unsuitable[16)]. This is because in the hydrolysed form they are readily soluble in aqueous medium. The observation that the copolymer salt **(I)** showed Nernstian response to sodium encouraged the authors to carry out intensive studies on various cations carrying different valency charges. Details of the preparation procedures and chemical characteristics of the various forms of the anhydride copolymer synthesized in our laboratory are included in another presentation (Dddamba *et al*) [16)].



(I)

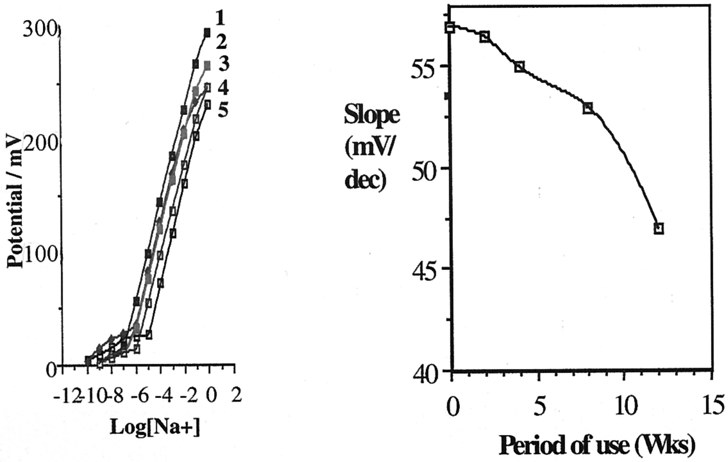
Structure (**I**): Difurylmethane-maleic anhydride copolymer sodium salt

Preparation of the Difurylmethane-maleic anhydride-PVC-CWE

The procedure used for the preparation of CWE involved mixing weighed amounts of the copolymer and PVC, grinding the mixture and adding a solution of dibutylphthalate (DBP) in tetrahydrofuran (THF). The % membrane composition with respect to the copolymer, PVC and DBP was varied as follows: (i) 18:15:65, (ii) 20:20:60, (iii) 20:50:30, (iv) 30:70:0 and (v) 70:30:0. A 20g mixture (enough for about 10 electrodes) was dissolved in 1 ml THF and the mixture left to stir overnight in a closed sample tube. Prior to coating, the metal wire was first cleaned with a sand paper (mild grade), rinsed with distilled-deionized water and wiped with a piece of tissue paper soaked in acetone. The coating procedure involved dipping a piece of silver wire (99.99 %, 4cm and 1.0 mm) in the membrane mixture and leaving it to dry in air for 2-3 minutes. The dipping procedure was repeated until a clearly visible film was formed on the silver wire. The membrane film was left to dry overnight in air. Prior to taking any measurements, the CWE was conditioned by soaking it in a 1.0 M solution of the analyte cation for at least two hours, followed by rinsing with distilled-deionized water. Between measurements, the electrode was stored in the soaking solution. The CWE was used as the working electrode and the bare wire as the reference electrode. The two electrodes were each connected to the pH/mV-meter using alligator clips. Potential readings of the cation standards were taken after 30sec for concentrations $> 10^{-3}$ M and 2 min for concentrations $< 10^{-3}$ M, equilibration times.

Response Characteristics of the Difurylmethane-maleic anhydride -CWE

The effect of membrane composition on the electrode performance was investigated by varying the % composition of the copolymer, PVC matrix and dibutylphthalate plasticizer (i - v above). Results (Fig. 1) showed that too much ion-exchanger (copolymer) with too little PVC matrix resulted in poor electrode performance. The presence of the plasticizer was shown to be necessary. In general, electrode 2 with a composition of 20 % copolymer, 20 % PVC and 60 % plasticizer, had the best sensitivity of 57 mV per decade change in analyte concentration (mV /dec), the lowest detection limit of 5 x 10^{-8} M and the best (widest) working range for cation concentrations. The lifetime of the electrode with a membrane composition of 20:20:60 was investigated by studying the calibration behaviour of Na^+ standards after varying lengths of use. The calibration plots were prepared every week for 12 weeks. The results (Fig. 1b) show that sensitivity decreased from 57 mV to 56.5 mV/dec after the second week, to 55 mV after 4 weeks and further to 47 mV/dec



(a) (b)

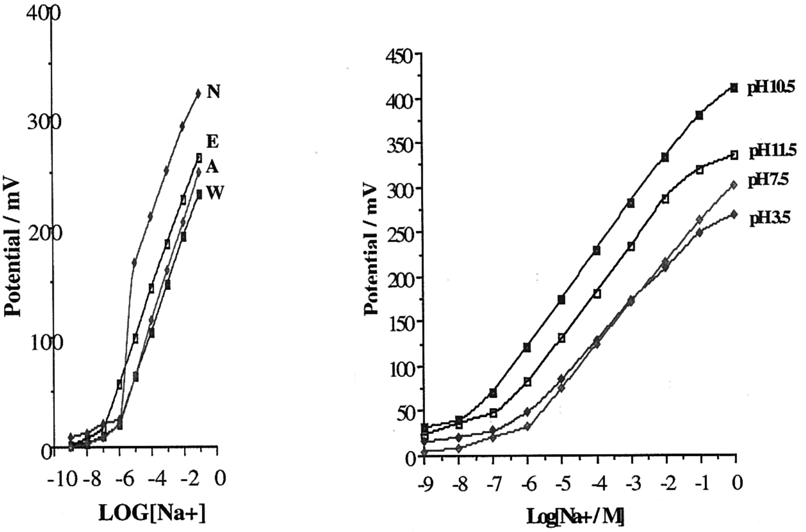
Fig.1 (a) Shows the effect of membrane composition on the sensitivity of calibration plots for Na^+ standards (1 x 10^{-9} – 1 x 10^0) in triethanolamine buffer (0.5 M, pH 10.5): (1) 18:15:65, (2) 20:20:60, (3) 20:50:30, (4) 30:70:0, and (5) 70:30:0- for % copolymer, % PVC and % DBP.

(b) Shows the effect of calibration sensitivity (slope) on the repeated use of DFM-MAH electrode over a period of time: slope values of Na^+ standard calibrations (5 x 10^{-8} - 1 x 10^0 M) versus time of electrode use (weeks).

after 12 weeks. This shows that the lifetime of the electrode is about 8 weeks, beyond which the sensitivity (slope) drops significantly.

Results of the investigation into coat thickness showed that there was no significant effect on the performance characteristics of the electrodes, as demonstrated by a % RSD value of 0.6 (n = 5) which falls within the precision range (0.5 - 2.5 %) obtained for replicate measurements with the same electrode. A slight variation in reproducibility (2.0 %, n = 5) of the electrode preparation procedure was observed. However, the error was less than 5 % (maximum acceptable error).

In order to study the effect of the background solution, four solutions were studied namely, ammonium carbonate (0.05M, pH 9.0), triethanolamine (0.5M, pH 10.5), nitric acid (0.001M, pH 3.0) and distilled-deionized water. In the preliminary investigation, ammonium carbonate buffer was found to form metal-carbonate precipitates with most of the di- and tri-valent cations as well as with Ag^+, as white deposits, on the electrode surface. This resulted in some loss of sensitivity. The alkali metal ions gave comparable results to those obtained with triethanolamine buffer. It is to be noted that the presence of NH_4^+ in the ammonium carbonate buffer was taken into account when preparing the calibration plots. The nitric acid background solution, on the other hand, showed inconsistent results for alkali metal calibrations. This is demonstrated (Fig. 2a) by a drastic change in sensitivity for the concentration range 1×10^{-6} M- 1×10^{-5} M. This behaviour may be explained by the low pH (3.0) which may possibly cause instability of the copolymer salt (see the previous section on copolymer hydrolysis). Thus, relatively poorer detection limits (1×10^{-6} M compared to 5×10^{-8} M given by triethanolamine medium) and sensitivity (45 compared to 57 mV/dec) values were observed. Distilled-deionised water used as the background solution, showed relatively poor detection limits (8×10^{-7} M) and sensitivity (42 mV /dec) for the Na^+ standard calibration. This observation can be explained by both the low pH and ionic strength of distilled–deionized water, since the Nernstian relationship applies for high ionic strength. Of the four media, it was the triethanolamine buffer that gave the best results, when considering factors such as cation-buffer interactions, ionic strength, pH and performance characteristics of the CWE. The optimum pH value, using triethanolamine buffer, was investigated. The normal pH of 0.5M triethanolamine in water is 10.5. When the pH of this solution was changed to pH 11.5, 7.5 and 3.5, the results obtained (Fig. 2b) for all the pH values, generally showed relatively poorer response characteristics than those obtained at pH 10.5.



(a) (b)

Fig. 2 (a) Shows the effect of the type of background solution on the sensitivity of calibration plots for Na^+ standards: N- nitric acid (0.001M, pH 3.0); E- triethanolamine (0.5 M, pH 10.5); A- ammonium carbonate (0.05 M, pH 8.9); W-distilled-deionized water.

(b) Shows the effect of pH of triethanolamine buffer on the sensitivity of calibration plots for Na^+ standards (1×10^{-9} to 1×10^{0} M) at pH values: 3.5, 7.5, 10.5 and 11.5.

The response characteristics of the electrode to different cations were studied by preparing calibration curves for different cations ($1 \times 10^{-9} - 1 \times 10^{0}$ M) using triethanolamine buffer at pH 10.5. Fig. 3 shows that the monovalent cations exhibited slightly better results in terms of detection limits, slopes of linear range and full working concentration range, compared to di- or tri- valent cations. The limit of detection was obtained as recommended by the analytical methods committee[17)]. The sensitivity values obtained showed a near-Nernstian response for most of the cations, ranging from 43 to 57, 23.0 to 27.5 and 14.8 to 18.5 mV/dec for mono-, di- and tri-valent cations, respectively. Generally, the performance characteristics were relatively better than those reported for either other fabricated[1-14)] electrodes or commercial[18)] electrodes. The precision of the electrode performance was investigated by obtaining replicate measurements (n = 5) for each cation with the same electrode. Electrodes with different membrane compositions were studied.

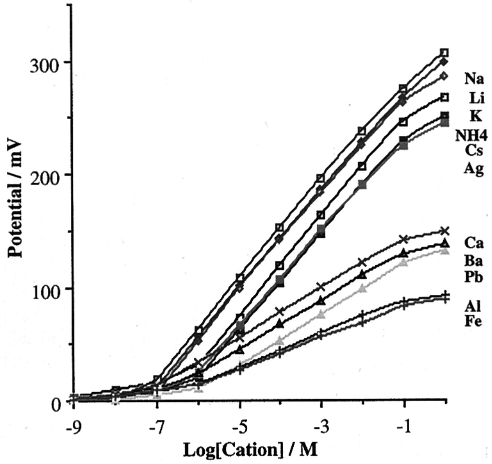


Fig. 3 Calibration plots for different cations (1×10^{-9} to 1×10^{0} M) in triethanolamine buffer.

Results in terms of % RSD values follow a similar trend to that obtained for the effect of membrane composition on the sensitivity of the calibration plots for Na^+ standards (see the beginning of this section). A summary of the results is given in Table 1.

Table 1: Summary of response characteristics for cations in triethanolamine buffer (pH 10.5) with a membrane of composition 20:20:60.

Cation	Detection limit (M)	Sensitivity (mV/dec)	Linear conc. range (M)	Full conc. range (M)	% RSD
NH_4^+	1 x 10^{-7}	52.5	5x10^{-7} -9x10^{-1}	1x10^{-7} -1 x 10^{0}	0.8
Li^+	8 x 10^{-8}	55.5	2x10^{-7}- 8x10^{-1}	6x10^{-8} -1x 10^{0}	0.6
Na^+	5 x 10^{-8}	57.0	2x10^{-7} -8x10^{-1}	5 x10^{-8} -1x 10^{0}	0.5
K^+	8 x 10^{-8}	55.0	1x10^{-7}- 7x10^{-1}	6x10^{-8}- 8 x10^{-1}	0.6
Cs^+	2 x 10^{-7}	51.0	5x10^{-7}- 5x10^{-1}	2x10^{-7} -8 x10^{-1}	0.9
Ag^+	5 x 10^{-7}	48.5	7x10^{-7}- 2x10^{-1}	5x10^{-7} -7 x10^{-1}	1.2
Ca^{+2}	7 x 10^{-7}	27.5	1x10^{-6}-2 x10^{-1}	7x10^{-7}- 5 x10^{-1}	0.8
Ba^{+2}	7 x 10^{-7}	26.0	1x10^{-6}- 2x10^{-1}	7x10^{-7} -5 x 10^{-1}	0.9
Pb^{+2}	8 x 10^{-7}	23.5	1x10^{-6}-2 x10^{-1}	8x10^{-7}- 3 x 10^{-1}	2.5
Al^{+3}	8 x 10^{-7}	18.5	3x10^{-6} -1x10^{-1}	8 x10^{-7} -2 x 10^{-1}	1.0
Fe^{+3}	9 x 10^{-7}	14.8	5x10^{-6}- 1x10^{-1}	9 x10^{-7}- 2 x 10^{-1}	2.0

Conclusions

The in-house synthesized DFM-MAH copolymer sodium salt has shown good qualities in terms of ion exchange properties. The electrode with the best membrane composition was found to comprise 20 % PVC, 20 % copolymer salt and 60 % plasticizer, as had a lifetime of 2 months. Exceptionally good limits of detection for the cations were obtained using triethanolamine buffer as the background solution. These values are better by a factor of 50-100 than those usually observed using commercial ion selective electrodes (typical range 1 x 10^{-6}– 5 x 10^{-6} M). The wide working range is particularly advantageous for the determination of a wide ranged sample concentration. The universal response to various metal ions carrying different charges implies that the electrode could be used as a detector for the chromatographic separation of cations.

In addition to the copolymer being used as a membrane for ion-selective electrodes, it may also be used as an ion-exchanger material for a chromatgraphic stationary phase. The next part of this work will be to study the electrode in a potentiometric flow-injection system, for the detection of cations, and its application as a chromatographic post-column detector.

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