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The use of a phenylpyrazine liquid crystalline material with a liquid crystalline solvent mediator as an ion-selective electrode

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Liquid crystalline 2-*n*-hexyloxy-5-(4-bromophenyl)-pyrazine was investigated as a novel neutral ionophore for use in ion selective electrodes. Two membrane compositions were studied. The first membrane included *o*-nitrophenyl octyl ether as a plasticising solvent mediator, and in the second membrane the plasticising mediator was replaced with a commercial non-ionophoric liquid crystal material (E7 Merck). The inclusion of E7, which exhibits solvent mediator properties, ensured the ionophore was present in a room temperature liquid crystalline phase. For membranes containing the E7, improved Nernstian response was observed for ammonium ions over the same concentration range, together with improved selectivity when used as ammonium and caesium selective electrodes. This is believed to be the first calamitic liquid crystalline ionophore polymer system described and may have potential in direct manipulation of ionophores in polymer membrane electrodes, using established liquid crystal switching technology.

The ionophores used in this study are members of a series of recently synthesised phenylpyrazine liquid crystals. These molecules were originally used to investigate the potential of pyrazine mesogens as highly birefringent materials for polymer dispersed switchable liquid crystal display devices.[1,2]

It became apparent that these materials had similar molecular structures to some neutral ion carriers that have been reported in the literature,[3] in addition to having potentially switchable mesogenic properties when incorporated into a room temperature liquid crystal host and dispersed in a polymer system. The host and ionophore would reorientate when subjected to an electric or magnetic field. The combination of these properties offered the possibility of preparing polymer electrode membranes utilising ionophores that may have their orientation controlled using known liquid crystal technology. This could alter their selectivity and provide information on the mechanism of ionophoric operation within the membrane. We wish to report at this stage details of the ionophoric properties of some of these materials. Their additional properties as liquid crystals and their exploitation in different membranes are currently under investigation and will be reported at a later date.

The initial objective was to investigate a number of pyrazine[1,2] based liquid crystal molecules by preparing a range of poly(vinyl chloride) PVC membranes and investigating their electrochemical properties in order to identify those that exhibited ionophoric behaviour and then characterise them in terms of their Nernstian response and selectivity coefficients.

Electrodes based on ion-sensitive membranes have often been found to respond to variations in ion activity in a Nernstian manner *i.e.* according to eqn. (1)

$$E_{\mathrm{I}} = E_{\mathrm{I}}^{0} + \frac{RT}{Z_{\mathrm{I}}F}\ln a_{\mathrm{I}} \qquad (1)$$

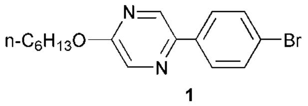
where a_{I} is the primary ion activity in the sample solution; E_{I} is the measured potential; E_{I}^{0} is the standard potential, R is the gas constant, T the absolute temperature, Z_{I} the charge on the primary ion and F the Faraday constant.

Ideally, a selective ionophore contained in a liquid or PVC membrane would respond to only one type of ion [the primary ion (I)]. In reality , all ion-selective electrodes respond to ions other than the primary ion . The effect of these interfering ions (J) on the membrane potential is given by eqn. (2), the Nikolskii–Eisenman equation:

$$E = E_{\mathrm{I}}^{0} + \frac{RT}{Z_{\mathrm{I}}F}\ln\left(a_{\mathrm{I}} + K_{\mathrm{IJ}}^{\mathrm{pot}}\cdot a_{\mathrm{J}}^{Z_{\mathrm{I}}/Z_{\mathrm{J}}}\right) \qquad (2)$$

The membrane composition was optimised and resulted in a PVC membrane incorporating 66 wt% of 2-nitrophenyl octyl ether (2-nPOE) as the solvent mediator (the choice of solvent mediator is particularly important where non-cyclic neutral carriers are used as these carriers have more orientational freedom within the membrane[4]), potassium tetrakis(4-chlorophenyl)borate as the anion exchanger and THF as the solvent. The film was cast by solvent evaporation and measurements were carried out using standard methods as outlined by Craggs, Moody and Thomas.[5]

A typical result using 2-*n*-hexyloxy-5-(4-bromophenyl)pyrazine (**1**) as a test carrier with an internal Cs^+ salt electrode filling solution was a near Nernstian response of 54.5 mV/concentration decade for Cs^+, 48.5 mV/concentration decade for NH_4^+ and 52 mV/concentration decade for K^+ with a linear range of four orders of magnitude. Based on a comparison of selectivity coefficients there was no significant interference from any ions tested. As the ammonium and potassium ions gave a near Nernstian response when measured separately, and have the same charge as the primary ion, use of the selectivity coefficient is valid when comparing the different membranes.[6] Selectivity coefficients were calculated using the Nikolskii–Eisenman equation above; they were experimentally determined using the separate solution method and are reported in Table 1.



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Liquid crystals (LC's) dispersed in polymers have been reported[7] and in order for them to be switchable at room temperature it is necessary for their LC phase to exist in that temperature range. The ionophore used in this study is liquid crystalline in the range of 55–71 °C (as a monotropic Smectic A

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Table 1 Selectivity coefficients for Cs^+ test electrode with 2-nitrophenyl octyl ether as plasticiser

Interfering ion (J)	Selectivity coefficient $\log K^{\mathrm{pot}}_{\mathrm{Cs}^+,\mathrm{J}}$
Li^+	−2.84
Na^+	−2.87
K^+	−1.27
NH_4^+	−1.60
Mg^{2+}	−3.48
Ca^{2+}	−3.40
Ba^{2+}	−2.62

Table 2 Selectivity coefficients for Cs^+ test electrode with E7 as plasticiser

Interfering ion (J)	Selectivity coefficient $\log K^{\mathrm{pot}}_{\mathrm{Cs}^+,\mathrm{J}}$
Li^+	−4.32
Na^+	−3.50
K^+	−2.56
NH_4^+	−2.73
Mg^{2+}	−3.21
Ca^{2+}	−3.74
Ba^{2+}	−3.69

Table 3 Selectivity coefficients for NH_4^+ test electrode with 2-nitrophenyl octyl ether as plasticiser

Interfering ion (J)	Selectivity coefficient $\log K^{\mathrm{pot}}_{\mathrm{NH}_4^+,\mathrm{J}}$
Li^+	−2.45
Na^+	−1.92
K^+	−0.35
Cs^+	1.95
Mg^{2+}	−1.60
Ca^{2+}	−2.80
Ba^{2+}	−1.23

Table 4 Selectivity coefficients for NH_4^+ test electrode with E7 as plasticiser

Interfering ion (J)	Selectivity coefficient $\log K^{\mathrm{pot}}_{\mathrm{NH}_4^+,\mathrm{J}}$
Li^+	−3.10
Na^+	−2.78
K^+	−0.76
Cs^+	1.10
Mg^{2+}	−3.30
Ca^{2+}	−3.52
Ba^{2+}	−2.56

phase); this range was lowered to room temperature by dissolving the ionophore in a commercial room temperature non-ionophoric nematic LC mixture E7. This was obtained from Merck UK Ltd and is a mixture based on 4-*n*-alkyl-4′-cyanobiphenyls, the exact composition has been previously reported in the literature.[8] The aim was to produce PVC and other polymer electrode membranes that have dispersed in them a liquid crystalline ionophoric mixture, and to evaluate their mesogenic and ionophoric characteristics. This was carried out by replacing the plasticiser (2-nPOE) used in the preparation of the previous membranes with an equivalent amount of the room temperature liquid crystal E7 (Merck UK Ltd). Suitable blanks were run without the ionophore to establish that the E7 did not exhibit ionophoric properties and that the E7 still retained its liquid crystal nematic phase properties when dispersed in the polymer.

The new membrane produced a better ion selective electrode for caesium in terms of selectivity. The electrode showed a response of 55 mV/concentration decade for Cs^+, 52 mV/concentration decade for NH_4^+ and 53 mV/concentration decade for K^+ with a linear range of four orders of magnitude. Selectivity coefficients are given in Table 2, which are very similar to the best caesium electrodes currently available. The improved performance for the liquid crystal mediated membrane may arise as a result of enhanced orientational freedom in the room temperature liquid crystal nematic phase for the phenylpyrazine ionophore. This is only one of several possible explanations for the improved performance, which may be better understood as the investigation of the mode of ionophoric operation progresses.

When the internal electrode filling solution was an ammonium salt solution, the electrode membrane material could be used as an ammonium ion selective electrode. The Nernstian response with E7 as solvent mediator is 58.5 mV/concentration decade for NH_4^+. The electrode has only a small amount of interference from potassium ions but cannot be used in the presence of caesium ions. Selectivity coefficients for these electrodes are given in Tables 3 and 4.

Both of the electrodes evaluated in this study exhibited very good time response characteristics, the time constants were in the order of three seconds and little if any equilibration time was required. They were stable in moderately acid media; however, alkaline conditions had a deleterious effect on the electrode, and for analytical work the sample should be buffered to around pH 5. The Nernstian response and selectivity coefficients were reproducible between batches. There was no significant drift within the timescale of the experiment, the electrode had a stable response for at least thirty days and should be stored dry after use.

Examination of the liquid crystalline solvent mediated membrane using polarising optical hot-stage microscopy showed a nematic texture which remained until the polymer was heated to 54 °C. This then reappeared upon cooling at 45 °C. When further investigated with a high powered optical microscope there did not appear to be much evidence for droplet formation. DSC examination of this polymer system and the E7 showed that the liquid crystal transitions of the E7 mixture alone were not obviously evident in the polymer/E7 membrane, possibly indicating that there is little phase separation and that E7 and the PVC were intimately mixed.

Studies of the switching effects on the dispersed liquid crystal ionophores of this and other liquid crystalline ionophores in various polymer systems whilst they are involved in ionophoric operation are in progress and will be reported in due course. It is hoped that this may allow us to externally vary the response and selectivity of membrane and give some indication of the mechanism of ionophoric action.

Notes and references

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