

# Studies of Spectrophotometric Reagents in Some Transition Metal and Lead Ion-selective Electrodes

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The general performance of ten spectrophotometric reagents, namely salicylaldehyde, 2,2'-dipyridyl, dimedone, 8-hydroxyquinoline, dithiooxamide, cupferron, nioxime, 4-methyl-nioxime, 1,10-phenanthroline hydrate and  $\alpha$ -benzoin oxime, as active sensors for  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Pb}^{2+}$  ions in a poly(vinyl chloride) membrane electrode system has been assessed using dioctyl phenyl phosphonate as plasticizing solvent mediator. Of the ten ionophores studied, four, namely salicylaldehyde, 2,2'-dipyridyl, dimedone and 8-hydroxyquinoline, showed good response to  $\text{Pb}^{2+}$  ions with the working concentration range from  $1 \times 10^{-6}$  to  $1 \times 10^{-1}$  mol dm $^{-3}$ . The best response to  $\text{Cu}^{2+}$  ions was shown by electrodes based on 2,2'-dipyridyl, dithiooxamide and cupferron. Although the electrode with 8-hydroxyquinoline as the active sensor responded very well to  $\text{Fe}^{3+}$ , the complex formed leached into solution. The most promising of the ionophores for the fabrication of  $\text{Ni}^{2+}$  ion-selective electrodes were found to be salicylaldehyde and cupferron with linear slopes of 32.9 and 22.5 mV per decade, respectively, from  $1 \times 10^{-4}$  to  $3.2 \times 10^{-2}$  mol dm $^{-3}$ .

**Keywords:** Spectrophotometric reagent; transition metal; ionophore; ion-selective electrode; membrane electrode

Ion-selective electrodes (ISEs) in a polymeric matrix based on various ionophores are well established for alkali and alkaline earth metals.<sup>1</sup> The selection of suitable ionophores for ion sensing can be helped by structural studies on the interaction between ionophores and ions. In this respect, macrocyclic and non-macrocyclic compounds have attracted widespread attention owing to the unique properties of these types of compounds.<sup>2</sup>

Much interest has been shown in using both macrocyclic<sup>3,4</sup> and non-macrocyclic<sup>2,5</sup> compounds as ionophores in a solvent polymeric membrane for transition metal ISEs, mainly for copper ISEs. Several known spectrophotometric reagents that complex with some transition metals have also been investigated as potential ionophores for transition metal ISEs.<sup>6,7</sup> The membrane electrodes responded very well to  $\text{Pb}^{2+}$  ions and to other transition metal ions such as  $\text{Cu}^{2+}$ .<sup>6,7</sup>

This paper describes an investigation into the use of ten well-known spectrophotometric reagents as potential ionophores in poly(vinyl chloride) (PVC) membrane electrodes for  $\text{Pb}^{2+}$  and some transition metal ions.

## Experimental

### Chemicals

With the exception of  $\text{Pb}(\text{NO}_3)_2$ , which was AnalaR grade, all solutions were prepared from salts of laboratory-reagent grade (BDH, Poole, Dorset, UK) using doubly distilled water. The chlorides of the metals were used, except for Pb when the nitrate was used.

### Ionophores and Membrane Materials

The ionophores studied are shown in Fig. 1. 5,5-Dimethyl-cyclohexane-1,3-dione (dimedone), salicylaldehyde, cyclohexane-1,2-dione dioxime (nioxime), 4-methylcyclohexane-1,2-dione dioxime (4-methyl-nioxime), 8-hydroxyquinoline and dithiooxamide were of laboratory-reagent grade and obtained from BDH. Cupferron [*N*-nitrophenyl-hydroxylamine (ammonium salt)] and 1,10-phenanthroline hydrate were also obtained from BDH but were of AnalaR

grade. 2,2'-Dipyridyl (general reagent grade) was obtained from Chemapol (Prague, Czechoslovakia) and  $\alpha$ -benzoin oxime of analytical-reagent grade was obtained from Merck (Darmstadt, Germany).

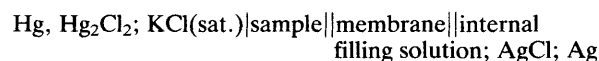
High relative molecular mass PVC was obtained from Fluka (Buchs, Switzerland); dioctyl phenyl phosphonate (DOPP) was obtained from Lancaster Synthesis (Lancaster, UK). Freshly distilled tetrahydrofuran (THF) (AnalaR, BDH) was used.

### Membrane Preparation

The general procedure used to prepare the PVC membrane was to mix 90 mg of PVC powder and 9 mg of the ionophore with 201 mg of DOPP as solvent mediator.<sup>6,7</sup> The mixture was stirred until the PVC was wet. Then, 3.0 cm $^3$  of THF were added to the mixture, which was stirred for 20 min on a magnetic stirrer. The THF solution was poured into a glass ring of 45 mm internal diameter on a glass plate and stored for 2 d at 28 °C. A disc of 13 mm diameter was cut with a cork-borer and fixed to a PVC tube with a solution of PVC in THF as adhesive. The PVC tube with the membrane was fixed onto an assembled electrode. The electrodes were conditioned in a  $1 \times 10^{-3}$  mol dm $^{-3}$  solution of the respective metal ion.

### Measurements

All measurements were made at  $24 \pm 1$  °C with cells of the type:



Metal chlorides ( $1 \times 10^{-3}$  mol dm $^{-3}$ ) were used as the internal filling solution, except for Pb where the internal filling solution was  $1 \times 10^{-3}$  mol dm $^{-3}$   $\text{Pb}(\text{NO}_3)_2$  and  $1 \times 10^{-3}$  mol dm $^{-3}$  NaCl. With the exception of Pb, for which the nitrate was used, all the sample solutions were prepared from the chloride salts of the metal ions.

The performance of the electrodes was investigated by measuring the e.m.f. values of the metal ion solutions over a concentration range from  $1 \times 10^{-6}$  to  $1 \times 10^{-1}$  mol dm $^{-3}$  by adding successive aliquots of known concentrations of the metal ion to 100 cm $^3$  of doubly distilled water.<sup>1</sup> The solutions

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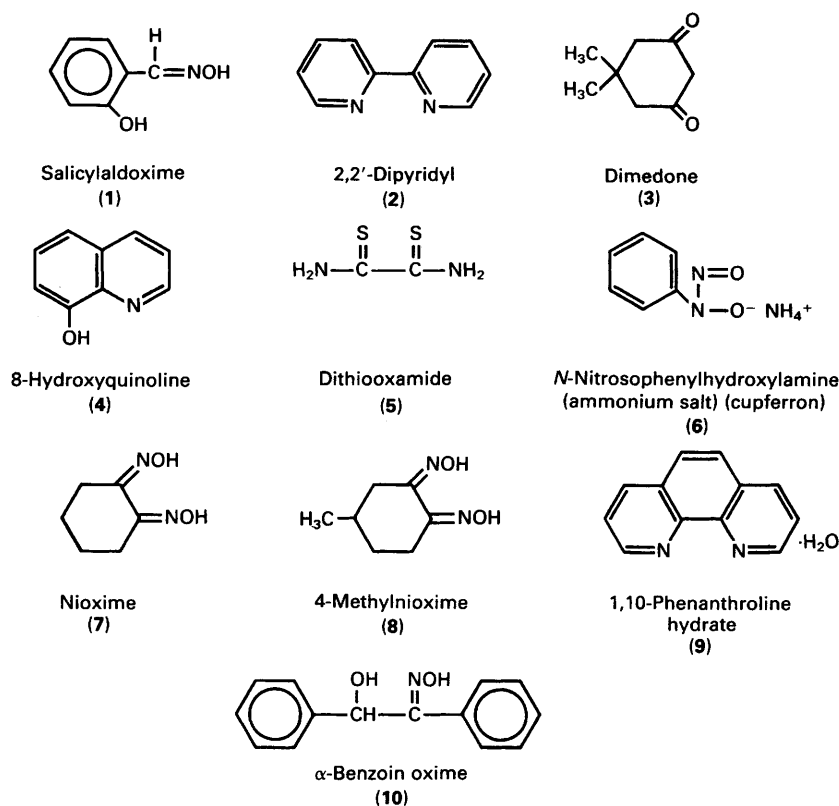


Fig. 1 Structures of ionophores 1–10

were stirred and the potential readings recorded when they became stable and then plotted as a logarithmic function of the cation activity. The activities of the metal ions were based on the activity coefficient ( $\gamma$ ) data calculated from the modified form of the Debye–Hückel equation, which is applicable to any ion<sup>2,4</sup>

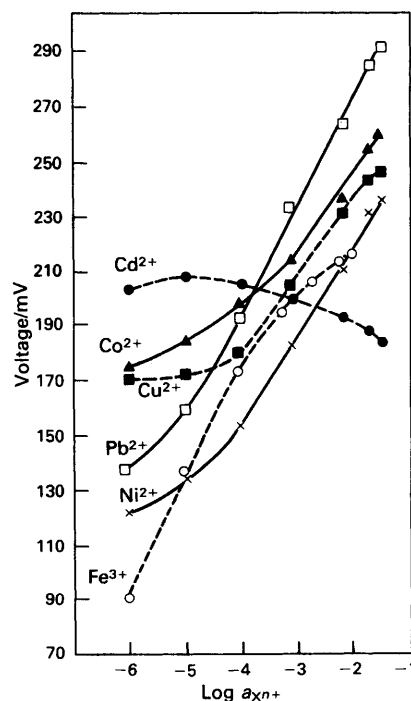
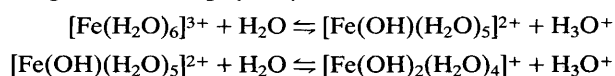
$$\text{Log } \gamma = -0.511Z^2 \left[ \frac{\sqrt{I}}{(1 + 1.5\sqrt{I})} - 0.2I \right] \quad (1)$$

where  $I$  is the ionic strength and  $Z$  the valency.

All e.m.f. measurements were obtained using a Pracitronic 870 mV digital pH meter (Messgeräte, Dresden, Germany).

### Results and Discussion

The membrane containing salicylaldoxime (ionophore 1) was responsive to  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Fe}^{3+}$  within the working concentration range from  $1 \times 10^{-6}$  to  $1 \times 10^{-1}$  mol  $\text{dm}^{-3}$  (Fig. 2). The responses to  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$ , which were linear, as indicated in Table 1, appear to be promising for the fabrication of ISEs. However, it was observed that a cream complex was formed on the membrane with  $\text{Cu}^{2+}$ , suggesting that the membrane was gradually being poisoned. The slope of 43.5 mV per decade for  $\text{Fe}^{3+}$  is also unusually large compared with the expected Nernstian response slope of 19.7 mV per decade for trivalent ions. The super-Nernstian slopes observed for the spectrophotometric reagent based ISEs for  $\text{Fe}^{3+}$  might be attributed to the presence of oxonium ions and the hydroxo species  $[\text{Fe}(\text{OH})_2(\text{H}_2\text{O})_4]^+$  and  $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ . This is because the  $\text{Fe}^{3+}$  ion is small, highly charged and hydrated and can undergo the following hydrolysis reactions:<sup>8</sup>

Fig. 2 Graph of voltage (mV) versus  $\log a_{X^{n+}}$  for the salicylaldoxime membrane electrodes

The best electrode response with the membrane based on salicylaldoxime was obtained for  $\text{Ni}^{2+}$  and  $\text{Pb}^{2+}$  with slopes of 32.9 and 38.9 mV per decade, respectively, and linear activity ranges from  $1 \times 10^{-4}$  to  $3.2 \times 10^{-2}$  and from  $3.2 \times 10^{-5}$  to  $3.2 \times 10^{-2}$  mol  $\text{dm}^{-3}$ , respectively.

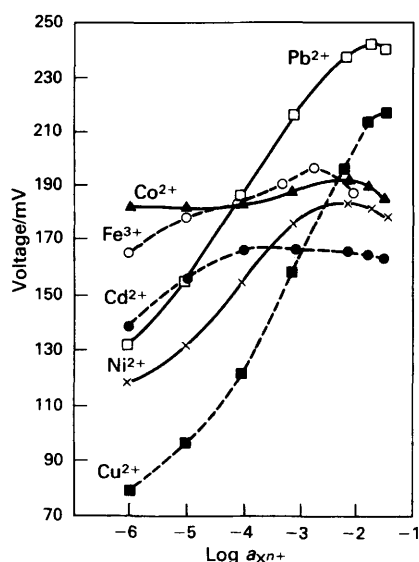
**Table 1** Response of various spectrophotometric reagent based PV membrane ISEs

Ionophore	Property*	Metal ISE					
		Fe <sup>3+</sup>	Cu <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cd <sup>2+</sup>	Pb <sup>2+</sup>
Salicylaldoxime†	S	43.5	27.4	28.8	32.9	—‡	38.9
	L	$1 \times 10^{-6}$ – $1 \times 10^{-4}$	$1 \times 10^{-4}$ – $2 \times 10^{-2}$	$7.9 \times 10^{-4}$ – $3.2 \times 10^{-2}$	$1 \times 10^{-4}$ – $3.2 \times 10^{-2}$	—	$3.2 \times 10^{-5}$ – $3.2 \times 10^{-2}$
2,2'-Dipyridyl	S	—	39.6	—	22.4	—	31.3
	L	—	$1 \times 10^{-4}$ – $1.8 \times 10^{-2}$	—	$1 \times 10^{-5}$ – $1.6 \times 10^{-3}$	—	$1 \times 10^{-5}$ – $3.2 \times 10^{-3}$
Dimedone	S	26.6	—	—	—	—	27.5
	L	$1 \times 10^{-4}$ – $7.9 \times 10^{-3}$	—	—	—	—	$1 \times 10^{-5}$ – $7.9 \times 10^{-3}$
8-Hydroxyquinoline	S	39.2	24.8	16.9	—	20.5	32.2
	L	$1 \times 10^{-6}$ – $7.9 \times 10^{-3}$	$5.6 \times 10^{-5}$ – $3.2 \times 10^{-2}$	$1 \times 10^{-5}$ – $6.9 \times 10^{-3}$	—	$1 \times 10^{-4}$ – $3.2 \times 10^{-2}$	$1 \times 10^{-5}$ – $7.9 \times 10^{-3}$
Dithiooxamide	S	44.4	34.0	—	25.1	—	—
	L	$9.1 \times 10^{-6}$ – $4.8 \times 10^{-4}$	$1 \times 10^{-4}$ – $3.2 \times 10^{-2}$	—	$1 \times 10^{-4}$ – $7.9 \times 10^{-3}$	—	—
Cupferron	S	47.5	28.9	18.1	22.5	14.4	—
	L	$1 \times 10^{-6}$ – $1.7 \times 10^{-3}$	$1 \times 10^{-4}$ – $3.2 \times 10^{-2}$	$3.2 \times 10^{-4}$ – $3.2 \times 10^{-2}$	$1 \times 10^{-4}$ – $3.2 \times 10^{-2}$	$1 \times 10^{-4}$ – $6.9 \times 10^{-3}$	—

\* S represents the slope in mV per decade; L represents the linear activity range in mol dm<sup>-3</sup>.

† The composition of this ionophore was 4.7% m/m.

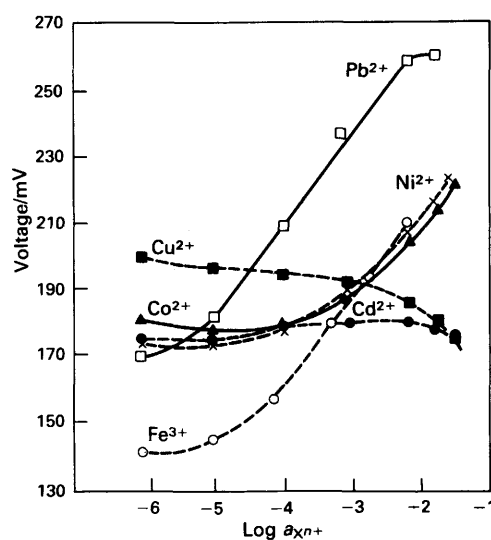
‡ — = non-linear response.



**Fig. 3** Graph of voltage (mV) versus  $\log a_{X^{n+}}$  for the 2,2'-dipyridyl membrane electrodes

The membrane containing 2,2'-dipyridyl (ionophore 2) gave linear slopes of 31.3 and 39.6 mV per decade with linear activity ranges from  $1 \times 10^{-5}$  to  $3.2 \times 10^{-3}$  and from  $1 \times 10^{-4}$  to  $1.8 \times 10^{-2}$  mol dm<sup>-3</sup> for Pb<sup>2+</sup> and Cu<sup>2+</sup>, respectively (Fig. 3). There were no appreciable responses to Fe<sup>3+</sup>, Co<sup>2+</sup> and Cd<sup>2+</sup>. Although the electrode responded to Ni<sup>2+</sup> with a slope of 22.4 mV per decade, the linear activity range of response was narrow (from  $1 \times 10^{-5}$  to  $1.6 \times 10^{-3}$  mol dm<sup>-3</sup>).

The only metal ions that gave a linear response with the membrane containing dimedone (ionophore 3) were Pb<sup>2+</sup> and Fe<sup>3+</sup> (Fig. 4). A linear response with a slope of 27.5 mV per decade was obtained for Pb<sup>2+</sup> over the activity range from  $1 \times 10^{-5}$  to  $7.9 \times 10^{-3}$  mol dm<sup>-3</sup>. For Fe<sup>3+</sup> a linear slope of 26.6 mV per decade in the activity range from  $1 \times 10^{-4}$  to  $7.9 \times 10^{-3}$  mol dm<sup>-3</sup> was obtained. Although the membrane responded to Ni<sup>2+</sup> and, to some extent, to Co<sup>2+</sup> the responses were not linear. There was no significant response to Cd<sup>2+</sup> and Cu<sup>2+</sup>.



**Fig. 4** Graph of voltage (mV) versus  $\log a_{X^{n+}}$  for the dimedone membrane electrodes

As indicated in Table 1 the membrane containing 8-hydroxyquinoline (ionophore 4) gave good responses to Pb<sup>2+</sup>, Fe<sup>3+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup> and Cu<sup>2+</sup> (Fig. 5). The membrane, however, forms a soluble complex with Fe<sup>3+</sup> in aqueous solution. The ionophore therefore washes out of the membrane and as a result the electrode has a short lifetime. The 8-hydroxyquinoline also forms a yellowish green complex on the membrane with aqueous Cu<sup>2+</sup> solution. The best electrode response using 8-hydroxyquinoline was to Pb<sup>2+</sup> with a slope of 32.2 mV per decade and in the activity range from  $1 \times 10^{-5}$  to  $7.9 \times 10^{-3}$  mol dm<sup>-3</sup>.

The membrane containing dithiooxamide (ionophore 5) responded favourably to Fe<sup>3+</sup>, Cu<sup>2+</sup> and Ni<sup>2+</sup>, in linear activity ranges from  $9.1 \times 10^{-6}$  to  $4.8 \times 10^{-4}$ ,  $1 \times 10^{-4}$  to  $3.2 \times 10^{-2}$  and  $1 \times 10^{-4}$  to  $7.9 \times 10^{-3}$  mol dm<sup>-3</sup> and with slopes of 44.4, 34.0 and 25.1 mV per decade, respectively (Fig. 6). The Cu<sup>2+</sup> ion gave the best electrode response with a slope of 34.0 mV per decade in the activity range from  $1 \times$

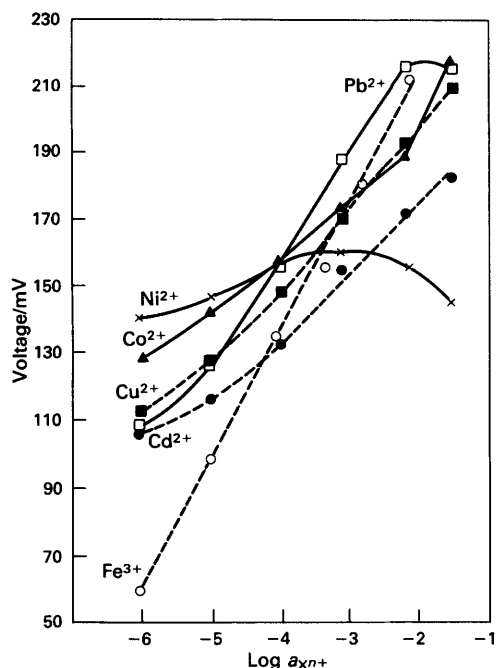


Fig. 5 Graph of voltage (mV) versus  $\log a_{X^{n+}}$  for the 8-hydroxyquinoline membrane electrodes

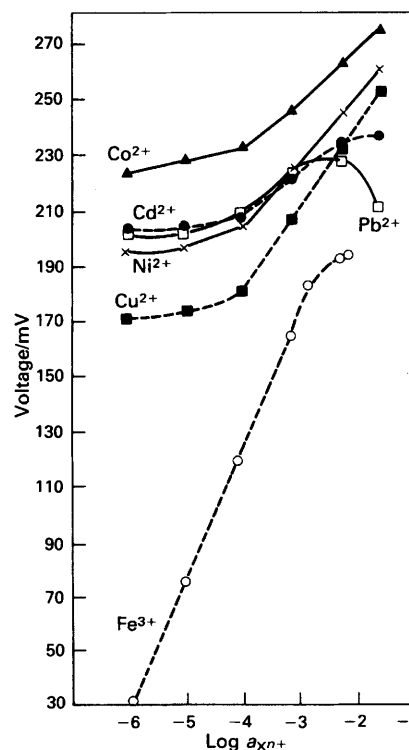


Fig. 7 Graph of voltage (mV) versus  $\log a_{X^{n+}}$  for the cupferron membrane electrodes

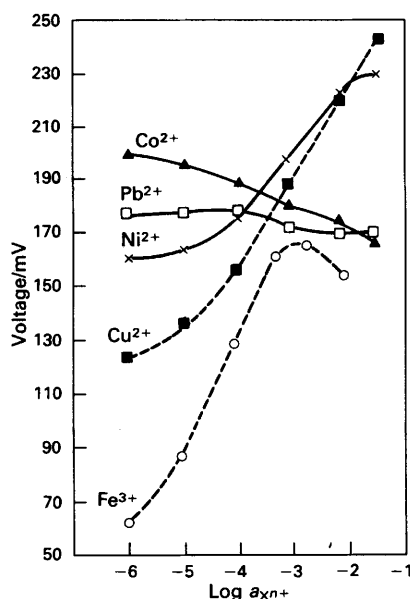


Fig. 6 Graph of voltage (mV) versus  $\log a_{X^{n+}}$  for the dithioamide membrane electrodes

$10^{-4}$  to  $3.2 \times 10^{-2}$  mol dm $^{-3}$ . It was observed that the membrane containing dithioamide was slightly coloured (yellowish brown).

The membrane electrode containing cupferron (ionophore 6) showed a linear response in the activity range from  $1 \times 10^{-6}$  to  $1.7 \times 10^{-3}$  mol dm $^{-3}$  for Fe $^{3+}$  with a slope of 47.5 mV per decade (Fig. 7). It also showed a linear response in the activity ranges from  $1 \times 10^{-4}$  to  $3.2 \times 10^{-2}$ ,  $1 \times 10^{-4}$  to  $3.2 \times 10^{-2}$  and  $3.2 \times 10^{-4}$  to  $3.2 \times 10^{-2}$  mol dm $^{-3}$  with slopes of 28.9, 22.5 and 18.1 mV per decade, respectively, for Cu $^{2+}$ , Ni $^{2+}$  and Co $^{2+}$ . The response to Cd $^{2+}$  with a slope of 14.5 mV per decade occurred in the linear activity range from  $1 \times 10^{-4}$  to  $6.9 \times 10^{-3}$  mol dm $^{-3}$  (Table 1).

Generally, the ionophores 1,10-phenanthroline (9), nioxime (7), 4-methylnioxime (8) and  $\alpha$ -benzoin oxime (10) did

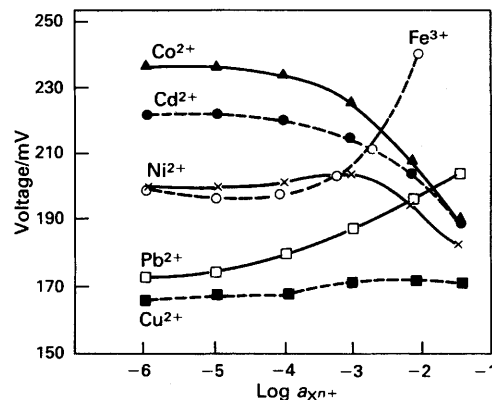


Fig. 8 Graph of voltage (mV) versus  $\log a_{X^{n+}}$  for the membrane with no ionophore

not give useful results, with 1,10-phenanthroline giving the worst response. In most instances the electrodes based on 1,10-phenanthroline responded at high concentrations giving negative slopes. This might be due to negative interferences from the anions of the salts used. In spite of the poor response to the metal ions studied by the electrodes based on these ionophores, the response slope of 20 mV per decade for Cu $^{2+}$  in the linear activity range from  $1 \times 10^{-4}$  to  $3.2 \times 10^{-2}$  mol dm $^{-3}$  is worthy of note. Nioxime and 4-methylnioxime formed purple complexes with aqueous Ni $^{2+}$  solutions and leached into solution.

In order to ascertain that these responses were due to the ionophores, responses of the membrane containing no ionophore to the metal ions were investigated. Fig. 8 shows the calibration graphs for Pb $^{2+}$ , Co $^{2+}$ , Cd $^{2+}$ , Ni $^{2+}$ , Cu $^{2+}$  and Fe $^{3+}$ . No appreciable response was observed for Co $^{2+}$ , Cd $^{2+}$ , Ni $^{2+}$  and Cu $^{2+}$ . The Pb $^{2+}$  ion gave a poor response while Fe $^{3+}$  showed some response at concentrations above  $1 \times 10^{-3}$  mol dm $^{-3}$ .

### Conclusion

Of the ten ionophores studied, salicylaldoxime, 2,2'-dipyridyl, dimedone and 8-hydroxyquinoline were found to have potential as ionophores for  $Pb^{2+}$  ISEs, and cupferron and salicylaldoxime potential as ionophores for  $Ni^{2+}$  ISEs. There were good linear responses to  $Cu^{2+}$  by most of the ionophores (*viz.*, salicylaldoxime, 2,2'-dipyridyl, 8-hydroxyquinoline, dithiooxamide, cupferron and nioxime). However, the major difficulty with some of these ionophores, particularly salicylaldoxime and 8-hydroxyquinoline, for  $Cu^{2+}$  might be with their life span.

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Paper 2/02912J

Received June 3, 1992

Accepted September 7, 1992