

Lithium Ion-selective Electrodes Based on 1,10-Phenanthroline Derivatives

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Polyvinyl chloride membrane electrodes based on 2,9-dialkyl-1,10-phenanthrolines exhibit excellent selectivity for Li^+ relative to Na^+ , K^+ , Mg^{2+} , and Ca^{2+} .

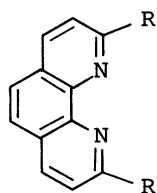
Much attention has been paid to the lithium ion-selective electrodes for environmental and biological applications. Several neutral carriers for Li^+ -selective electrodes have been reported so far, such as noncyclic polyethers, crown ethers and so on.^{1,2)} In this paper we report that PVC membrane electrodes based on 2,9-dimethyl-1,10-phenanthroline (1) and 2,9-dibutyl-1,10-phenanthroline (2) exhibit excellent selectivity for Li^+ over other alkali and alkaline earth metal ions.

Carriers, 2,9-dimethyl-1,10-phenanthroline 1 and 1,10-phenanthroline (3) were purchased from Wako Pure Chemical Industry Inc. 2,9-Dibutyl-1,10-phenanthroline 2 was prepared as described by Dietrich-Buchecker et al.³⁾ 2-Nitro-1-octyloxybenzene(NPOE) and potassium tetrakis(4-chlorophenyl)borate(KTCPB)⁴⁾ (Dojin Lab.) were used without further purification.

The polymeric membranes for the ion-selective electrodes were cast from tetrahydrofuran solutions of 1.5% carrier, 69.8% NPOE, 27.9% PVC, and 0.8% KTCPB. A disk of the polymeric membrane 5 mm in diameter was cut out from the membrane obtained and was then mounted on an electrode body. The emf measurements were carried out at 25°C; the composition of the electrochemical cell being $\text{Ag}/\text{AgCl}/10^{-2} \text{ mol dm}^{-3} \text{ LiCl}/\text{PVC membrane}/\text{sample solution}/0.1 \text{ mol dm}^{-3} \text{ NH}_4\text{NO}_3/\text{satd. KCl}/\text{AgCl}/\text{Ag}$. The potentiometric ion-selectivity coefficients $k_{i,j}^{\text{Pot}}$ (i is the primary ion; j is an interfering ion) were determined by the separate-solution method, using the Nicolsky-Eisenman equation(Eq.1), where R, a's, T, Z, and F denote gas constant, ion activities, absolute temperature, the charge of the ion, and Faraday constant, respectively.

$$E = E_i^\circ + \frac{2.3RT}{Z_i F} \log [a_i' + \sum_{i \neq j} k_{i,j}^{\text{Pot}} (a_j')^{Z_i/Z_j}] \quad (1)$$

The calibration curve obtained for the electrode based on carrier 2 was linear over the activity range 1.0×10^{-4} to 1 mol dm^{-3} with a slope of 53 mV for Li^+ . The response time of the electrodes was less than 0.5 min. The lifetime of the membrane was long enough for practical use, as was found for other PVC membranes.

Table 1. Selectivity coefficients of Li⁺-selective electrodes based on 1-3

Carrier	R	H ⁺	log $k_{Li, M}^{Pot}$				
			Li ⁺	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
1	CH ₃	2.2	0	-2.5	-3.0	-2.9	-2.9
2	CH ₃ (CH ₂) ₃	2.4	0	-3.2	-3.5	-3.2	-3.3
3	H	2.5	0	-0.71	-0.75	0.11	-0.44

The selectivity coefficients for Li⁺ relative to the ion M in the PVC membrane electrodes are listed in Table 1. In Table 1, electrodes based on carrier 1 and 2, which have methyl and butyl groups at 2,9- positions of phenanthroline respectively, exhibits excellent selectivity for Li⁺ over other metal ions. It should be noted that selectivity coefficient $\log k_{Li, Na}^{Pot} = -3.2$ of the electrode based on 2 is superior to those of previously described Li⁺-selective electrodes.^{1,5,6} On the contrary, electrode based on carrier 3, which have no substituent at 2,9- positions of phenanthroline, exhibits less Li⁺-selectivity than those based on 1 and 2. From these results, it seems to be important to introduce the substituents on adjacent carbons to nitrogens of phenanthroline for the appearance of high Li⁺-selectivity. The electrodes appear to be affected by an interference from H⁺ in acidic solutions, nonetheless the electrodes could be sufficiently utilized for Li⁺ determination in solution above pH 4.

The present electrode seems promising for the application to a clinical use, such as determination of Li⁺-ions in blood during the therapy of manic-depressive psychosis.^{5,7} 2,9-Dialkyl-1,10-phenanthroline derivatives will be used for further application such as Li⁺-indicating agent or extracting agent. Further investigation on the relationship between the nature of substituents and ion-selectivity is now in progress.

References

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