A Highly Selective Ionophore for Potassium Ions: a Lipophilic Bis(15-crown-5) Derivative

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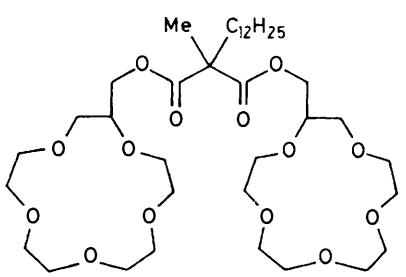
A bis(crown ether) of 15-crown-5 (**1**) bearing a long aliphatic chain is a promising K^+-selective ionophore for ion-selective electrodes.

Bis(crown ether) derivatives with a short aliphatic chain are likely to complex particular metal cations very strongly, the cation being sandwiched intramolecularly by two adjacent crown ether rings.[1–5] Such complexation by a bis(crown ether) becomes more specific than for the corresponding monocyclic crown ether for certain alkali metal cations whose sizes slightly exceed the size of the cavity of the crown ether rings.

We have synthesized a novel bis(15-crown-5) derivative (**1**), to obtain a highly efficient K^+-ionophore for ion-selective electrodes. Condensation of dodecyl methyl malonic chloride with hydroxymethyl-15-crown-5 (benzene, AgCN,[6] reflux) gave (**1**) (40%, colourless oil).†



(**1**)

The bis(crown ether) has been used as an ionophore for K^+-selective electrodes of the coated-wire type.[7]‡ The calibration plots possess a near-Nernstian slope for a wide range of K^+ activity (Figure 1) and the values of the selectivity coefficient (k_{KM}) demonstrate the excellent K^+-selectivity of the ionophore (Table 1). In particular, the k_{KNa} value is 2×10^{-4}, which is comparable to that for valinomycin, a naturally occurring K^+-ionophore. In the preference of K^+ over Rb^+ and Cs^+, the bis(crown ether) is superior to valinomycin.

The bis(crown ether) is also endowed with high lipophilicity, derived primarily from the dodecyl group, which is an important prerequisite for ionophores. Because of this lipophilicity stable e.m.f. readings (drift within 0.1 mV), and rapid response

† Satisfactory elemental analysis and spectral data were obtained for the bis(crown ether).

‡ The membrane with which a silver wire was coated contains (**1**), *o*-nitrophenyl octyl ether, and poly(vinyl chloride): 3.8, 64.2, and 32.0 wt%, respectively. The reference electrode was a calomel electrode combined with an agar bridge containing 0.1 M NH_4NO_3.

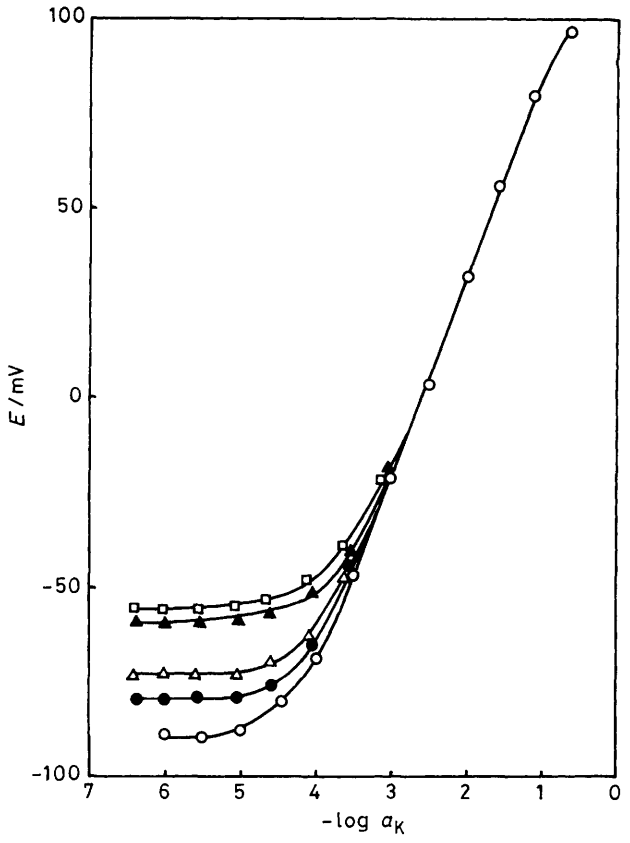


Figure 1. Response and selectivity of the K^+-selective coated-wire electrode based on the bis(crown ether) (**1**) at 25 °C. Calibration plots for KCl without interfering ions (○); selectivity curves in the presence of 1×10^{-2} M NH_4Cl (□), 1×10^{-3} M RbCl (▲), 1 M NaCl (△), and 1×10^{-3} M CsCl (●).

Table 1. Selectivity coefficients for K^+-selective electrodes based on bis(crown ether) (**1**) and valinomycin.

Ionophore	k_{KM}[a]			
	Na^+	Rb^+	Cs^+	NH_4^+
(**1**)	2×10^{-4}	2×10^{-1}	1×10^{-2}	4×10^{-2}
Valinomycin	1×10^{-4}	2	3×10^{-1}	4×10^{-2}

[a] Calculated from the selectivity curves in Figure 1 by a mixed solution method.

(less than 10 s by the incremental method) were recorded for the (**1**)-based K^+-selective electrode. The electrode also had a longer lifetime compared to that with the previously reported bis(crown ethers) of benzo-15-crown-5.[2] No deterioration was observed even after 200 measurements.

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