

Cesium-selective chemically modified field effect transistors with calix[4]arene-crown-6 derivatives

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Received 1 December 1994; revised 23 February 1995; accepted 26 February 1995

Abstract

Calix[4]arene-crown-6 derivatives (1–3) in the 1,3-alternate conformation, incorporated in poly(vinylchloride) membranes of CHEMFETs, exhibit good Cs⁺-selectivity and Nernstian behaviour. The Cs⁺-selectivity over Na⁺, i.e., $\log K_{\text{Cs,Na}}^{\text{pot}} = -3.3$, is slightly better than observed for bis(18-crown-6) derivatives ($\log K_{\text{Cs,Na}}^{\text{pot}} = -3.0$). The CHEMFETs respond sub-Nernstian in the presence of NH₄⁺ and K⁺. Model calculations show that this can be explained by the small difference between the stability constants of the Cs⁺- and K⁺-complexes and by the high partition coefficient of NH₄⁺ in favour of the membrane phase, respectively.

Keywords: CHEMFETs; Calix[4]arene-crown-6; Cesium

1. Introduction

Calix[4]arenes are versatile building blocks for the construction of selective ion receptors, because of the possibility to functionalize the phenolic oxygens with appropriate ligating groups. Calix[4]arenes modified with four ethyl ester or acetamide binding sites are selective for sodium ions even in the presence of a large excess of other alkali or alkaline earth metal ions [1]. Calix[4]arenes having two diametrically

substituted thioether functionalities are selective for Ag⁺, and those with four thioamide groups show preference for binding of Pb²⁺ [2]. When modified with a terphenyl group, the calix[4]arene can bind rubidium with remarkable kinetic stability, while 1,3-diethoxycalix[4]arenes with a crown-4 and crown-5 bridge at the remaining *syn*-distal positions show a high Na⁺/K⁺ and K⁺/Na⁺ selectivity, respectively [3–5]. The selectivity in metal ion binding not only depends on the ring size of the crown ether bridge of the calixarene but also on the conformation of the calixarene. For example, the partial cone conformation of the calix[4]arenes with the crown-4 and the crown-5 bridge shows a higher selectivity for the primary ion than the cone and the 1,3-alternate conformation.

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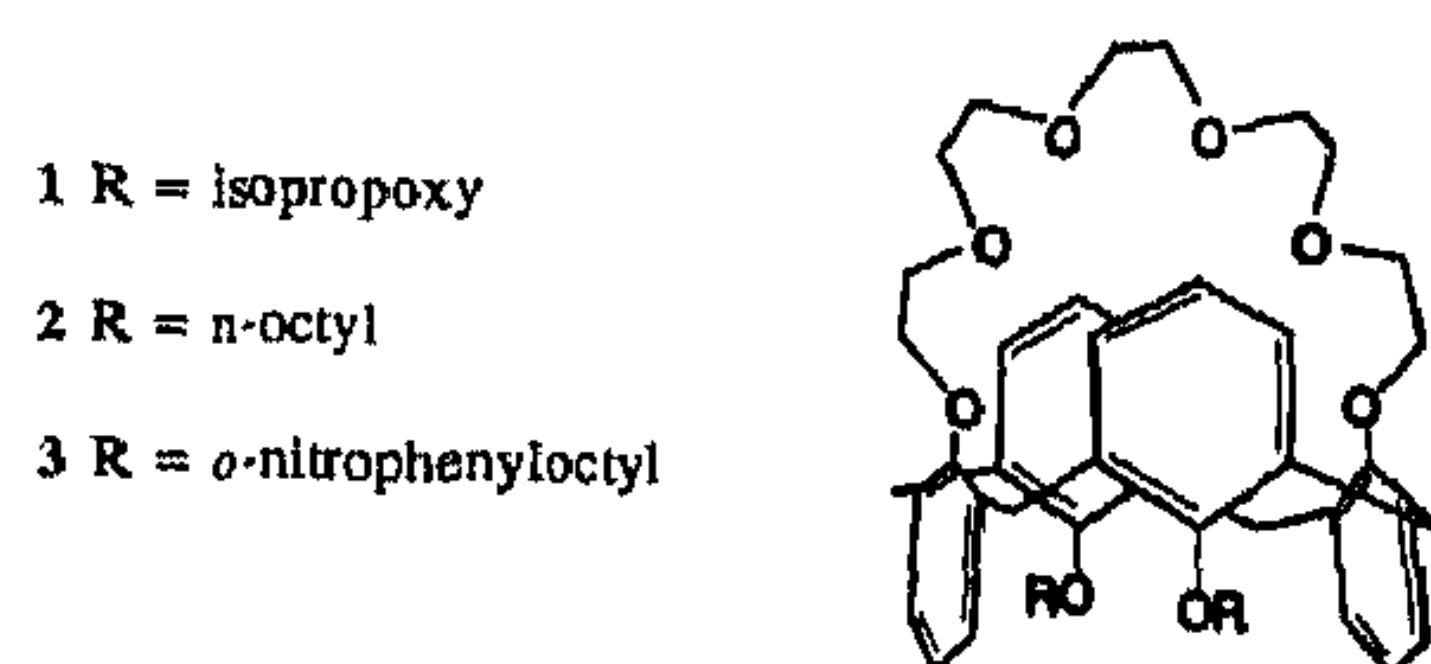


Fig. 1. Calix[4]arene-crown-6 derivatives in the 1,3 alternate conformation.

Recently, Ungaro et al. [6] found that 1,3-dialkoxycalix[4]arene-crown-6 derivatives in the 1,3-alternate conformation (Fig. 1) show a very high selectivity in the extraction of cesium over sodium ions. These calix[4]arene-crown-6 derivatives have been successfully applied in supported liquid membranes for the removal of cesium in the presence of sodium [7]. The preference of 1,3-dialkoxycalix[4]arene-crown-6 derivatives for binding of the cesium ion renders these compounds of interest as cesium-selective ion receptors in potentiometric sensors. The high selectivity of the compounds 1–3 can be explained by the preorganization of the ligand [8] and by the fact that the less polar 1,3-alternate conformation prefers to bind the “softer” cesium ion over the “hard” sodium ion [9]. Moreover the 1,3-alternate conformation allows interaction of the cesium ion with the π -electrons of two aromatic rings. It has already been shown that dibenzo-18-crown-6 derivatives are selective for cesium. These ionophores have been applied in ion selective electrodes [10–12]. In this paper we describe the application of calix[4]arene-crown-6 derivatives (1–3) in the 1,3-alternate conformation, as selective ionophores in chemically modified field effect transistors (CHEMFETs).

2. Experimental

2.1. Reagents

The cesium selective ionophores were prepared according to literature procedures [6]. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl before use. High-molecular-weight (HMW) PVC was obtained from Janssen Chimica; bis(2-ethylhexyl) sebacate (DOS), *ortho*-nitrophenyl

octyl ether (*o*-NPOE), and potassium tetrakis[3,5]-bis(trifluoromethyl)phenyl]borate (KTTFPB) were purchased from Fluka. The alkali and alkaline earth chlorides used were of analytical grade (Merck-Schuchardt), except cesium (Suprapur, Merck-Schuchardt). All solutions were made with deionized, doubly distilled water.

2.2. CHEMFETs

CHEMFETs were prepared from ISFETs with dimensions of 1.2×3 mm. Details of the fabrication of the ISFETs modified with poly(hydroxyethyl methacrylate) hydrogel (polyHEMA) have been described previously [13,14]. The modified ISFETs were mounted on a printed circuit board, wire bonded, and encapsulated with epoxy resin (Hysol H-W796/C8 W795). The polyHEMA-layer of the ISFETs was conditioned by immersion in an 0.1 M CsCl solution (pH 4, HCl) for 1 h, prior to solvent casting. The ion-sensitive membrane was casted on the polyHEMA hydrogel by adding one drop of THF solution containing 100 mg of a mixture composed of HMW-PVC (33 wt%), plasticizer (65.5%), ionophore (1 wt%), and KTTFPB (50 mol%, with respect to the ionophore) per ml of THF. The THF was allowed to evaporate overnight.

2.3. CHEMFET measurements

The output signal of the CHEMFETs was measured in a constant drain-current mode ($I_d = 100 \mu\text{A}$), with a constant drain-source potential ($V_{ds} = 0.5$ V). This was achieved using a CHEMFET amplifier of the source-drain follower type (Electro Medical Instrumentation, Enschede). The developed membrane potential was compensated by an opposite potential (ΔV_{gs}) via the reference electrode. A saturated calomel electrode (SCE) was used as reference, connected to the sample solution via a salt bridge filled with 1.0 M LiOAc. Ten CHEMFETs were monitored simultaneously and the data were collected and analyzed using an Apple IIGS microcomputer. Computer controlled switches allowed disconnection of CHEMFETs which showed a too high leakage current ($I_d \geq 50$ nA). All equipment was placed in a dark and grounded metal box in order to eliminate any effects from static electricity and pho-

tosensitivity of the CHEMFETs. The potentiometric selectivity coefficients, K_{ij}^{pot} , were determined by the fixed interference method (FIM). The constant background concentration of the interfering ion was 0.1 M. Before starting the measurements the CHEMFETs were conditioned in 0.1 M CsCl. All measurements were carried out by titration of 25 ml of 0.1 M interfering cation with 0.01 and 1.0 M CsCl solutions at a constant pH of 4. CHEMFETs were stabilized for 20–30 min after immersion in the interfering cation solution before starting the titration.

3. Results and discussion

CHEMFETs, with three different 1,3-dialkoxycalix[4]arene-crown-6 derivatives in the 1,3-alternate conformation (1–3) incorporated in the membrane gave a linear, near Nernstian response in the activity range $\log a(\text{Cs}^+) = -4.5$ to -1 in 0.1 M solutions containing calcium or sodium as interfering ions (Table 1). The interference of potassium and ammonium ions is more pronounced, and linear responses with slopes of about 40 mV decade⁻¹ were obtained in the range $\log a(\text{Cs}^+) = -3.0$ to -1 . The response of the CHEMFET incorporating 2 in the presence of 0.1 M NaCl solution is given in Fig. 2. The nature of the plasticizer has only little influence on the response characteristics. With *o*-NPOE as the plasticizer ionophore 2 gave a slightly better Cs/Ca and Cs/Na selectivity compared with DOS as plasticizer. In both cases the slope is Nernstian. The very similar behaviour of the three ionophores 1, 2, and 3 shows that the alkoxy groups at the opposite site of the crown ether ring have no significant effect. The

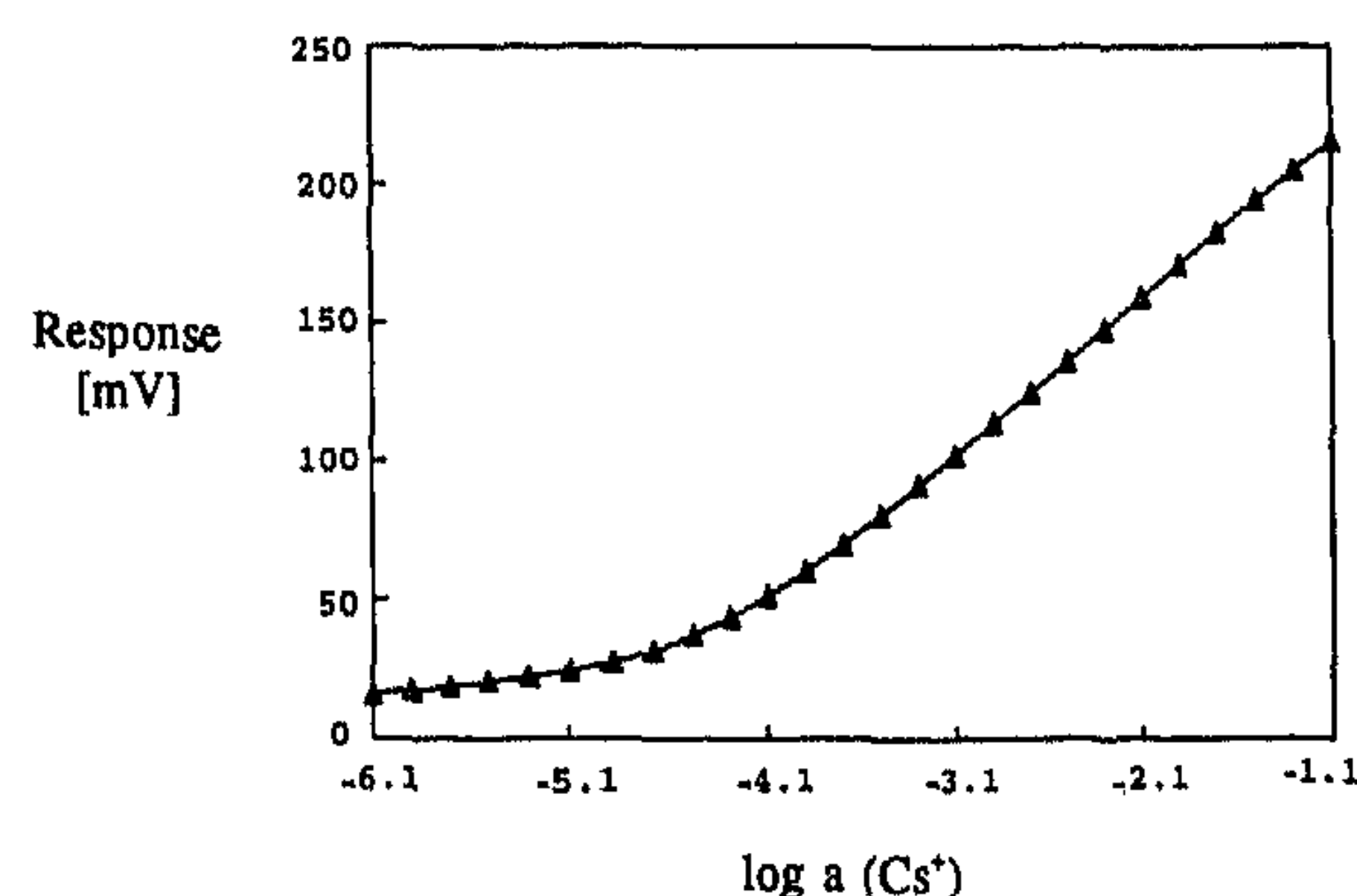


Fig. 2. Response of cesium-selective CHEMFET incorporating 2 in the presence of 0.1 M NaCl solution.

highest Cs/Na selectivity ($\log K_{\text{Cs,Na}}^{\text{pot}} = -3.3$, Table 1), is slightly better than that observed for bis(18-crown-6) derivatives (with 3 or 5 CH₂ between two crown ether moieties ($\log K_{\text{Cs,Na}}^{\text{pot}} = -3.0$) [10]. However, the latter were measured with ion selective electrodes which give generally higher selectivity coefficients than CHEMFETs. The sub-Nernstian response we observed with potassium as the interfering ion is probably due to the rather high stability constant of the ionophores with potassium. The difference in stability constant in methanol of 1 with potassium ($\log \beta = 4.3$) or with cesium ($\log \beta = 6.4$) is probably too small [7]. The sub-Nernstian response observed in the presence of ammonium ions in solution can be attributed to the higher partition coefficient of the ammonium ion to the membrane phase compared to the cesium. Although exact data for the partition of both ions between the aqueous phase and the membrane phase are not known, the free energy of transfer of the ammonium ion from water to a protic organic solvent is lower

Table 1

Results of CHEMFET measurements with different Cs⁺-selective calix[4]arene derivatives^a

Membrane material	Ionophore	log $K_{\text{Cs,j}}^{\text{pot}}$ and slope (mV/dec.) ^{b,c}			
		0.1 M Ca ²⁺	0.1 M Na ⁺	0.1 M K ⁺	0.1 M NH ₄ ⁺
PVC/DOS	1	-3.3 (57)	-3.3 (57)	-2.0 (40)	-1.9 (39)
PVC/DOS	2	-3.1 (60)	-3.0 (57)	-1.9 (40)	-1.9 (37)
PVC/DOS	3	-3.3 (57)	-3.3 (58)	-1.9 (39)	-1.9 (40)
PVC/ <i>o</i> -NPOE	2	-3.3 (58)	-3.3 (59)	-1.9 (40)	-1.9 (39)
PVC/ <i>o</i> -NPOE	3	-3.1 (56)	-3.3 (56)	-2.1 (41)	-2.1 (42)

^a 1 wt% ionophore and 50 mol% (with respect to ionophore) KTTFPB.

^b $\log K_{\text{Cs,j}}^{\text{pot}} \pm 0.1$.

^c Slope ± 2 mV dec.⁻¹[Cs⁺].

than that for the cesium ion. For example, $\Delta G_{tr}^0(\text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH})$ is 1.17 kcal/mol for NH_4^+ and 2.30 kcal/mol for Cs^+ [15]. A theoretical model, developed earlier [16,17], can be used for the simulations of the membrane potential. The influence of the membrane potential in presence of the primary ions can be simulated by variation of the association constant or the partition coefficient of interfering ions. The effect of divalent primary and interfering ions can also be described by this model. The effects of differences in the partition coefficient of the interfering cation are illustrated in Fig. 3, for an ionophore with an association constant of 10^9 M^{-1} for cesium and 10^5 M^{-1} for the interfering cation [16]. This figure shows that a good Nernstian behaviour can be expected when the partition coefficient of the interfering ion is lower or the same as the partition coefficient of the primary ion. This is for example the case for sodium, potassium, and calcium as the interfering ions. However, when the partition of the interfering ion is considerably higher (10^{-3}) than that of the primary ion (10^{-6}), a much lower sensitivity and selectivity is observed. The effect of differences in association constant of the interfering ion (β_2) is illustrated in Fig. 4. When the interfering ion has a considerably lower complexing ability (10^5 M^{-1}), which is for example the case for sodium, the response is Nernstian. However, when the associa-

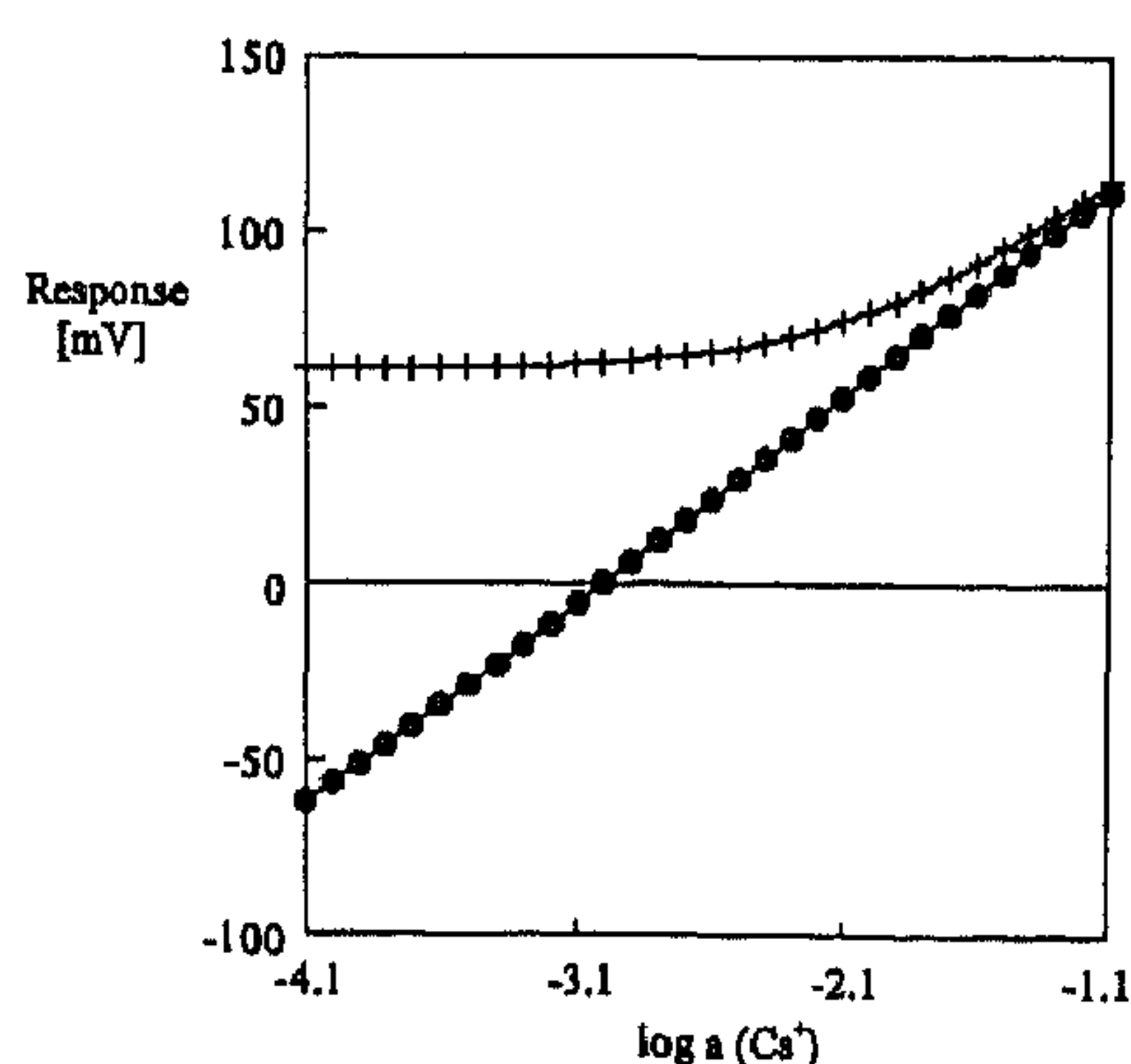


Fig. 3. The influence of the partition coefficient of the interfering cation, k_{+2} , on the potentiometric response. Concentration of ionophore 10^{-3} M ; anionic sites $5 \times 10^{-4} \text{ M}$; association constant β_1 is 10^9 M^{-1} for primary and 10^5 M^{-1} for interfering cation. (●) Partition coefficients of primary cations and interfering ion is 10^{-6} ; (+) partition coefficient of primary cation is 10^{-6} and of interfering ions are 10^{-3} .

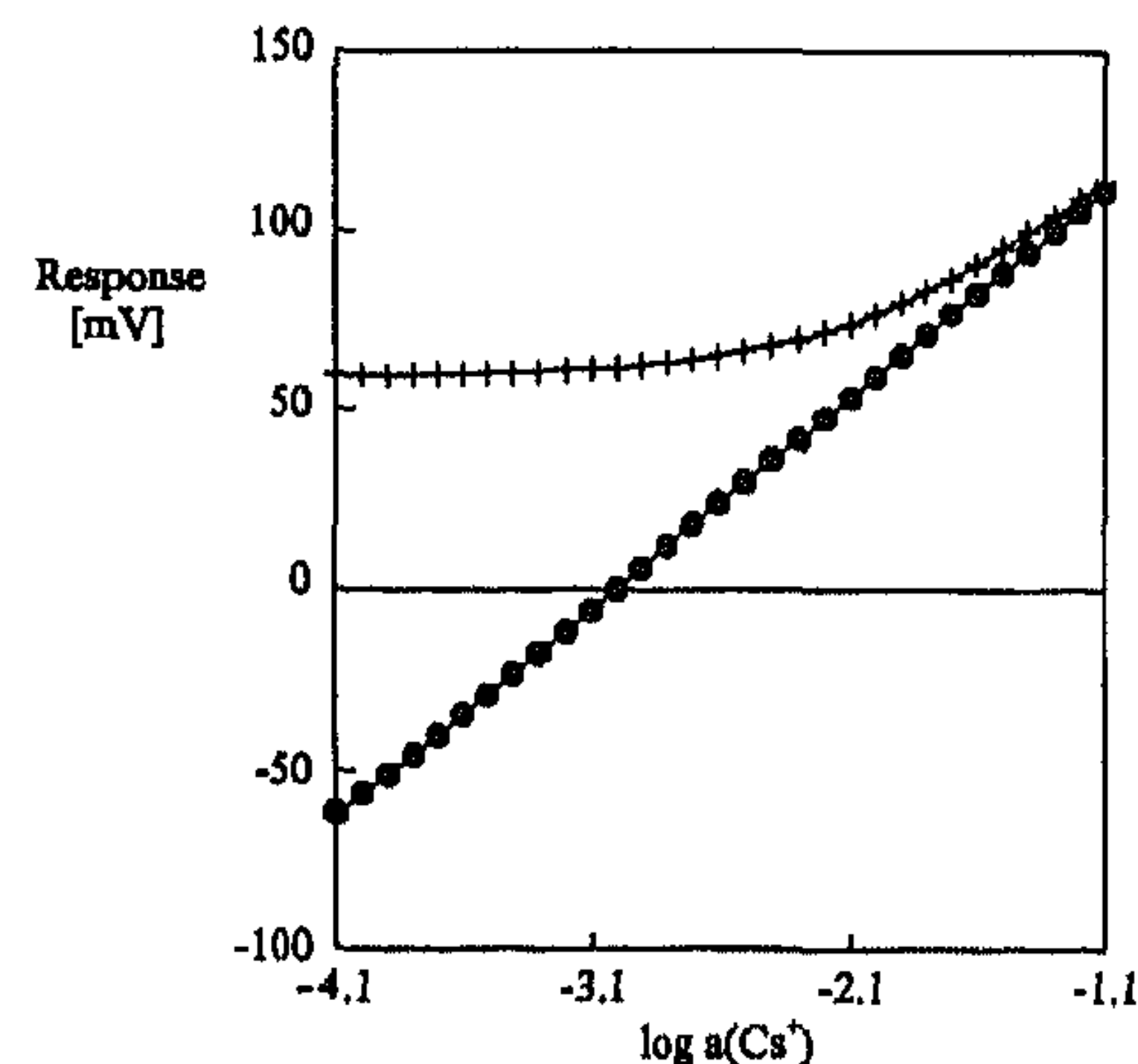


Fig. 4. The influence of the association constant β_2 on the potentiometric response. Concentration of ionophore concentration 10^{-3} M ; anionic sites $5 \times 10^{-4} \text{ M}$; association constant β_1 of primary cation, 10^9 M^{-1} ; partition to the membrane phase of cations and anions is 10^{-6} . (●) Association constant β_2 of interfering cation is 10^5 M^{-1} ; (+) association constant of interfering ion is 10^8 M^{-1} .

tion constant comes close (10^8 M^{-1}) to that of the primary ion, a lower sensitivity and selectivity can be observed.

References

- [1] J.A.J. Brunink, J.R. Haak, J.G. Bomer, M.A. McKerverey, S.J. Harris and D.N. Reinhoudt, *Anal. Chim. Acta*, 254 (1991) 75.
- [2] P.L.H.M. Cobben, R.J.M. Egberink, J.G. Bomer, P. Bergveld and D.N. Reinhoudt, *J. Am. Chem. Soc.*, 114 (1992) 10573.
- [3] W.I. Iwema Bakker, M. Haas, H.J. den Hertog Jr., W. Verboom, D. de Zeeuw and D.N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2*, (1994) 11.
- [4] J. Yamamoto and S. Shinkai, *Chem. Lett.*, (1994) 1115.
- [5] Z. Brzozka, B. Lammerink, D.N. Reinhoudt, E. Ghidini and R. Ungaro, *J. Chem. Soc., Perkin Trans. 2*, (1993) 1037.
- [6] R. Ungaro, A. Casnati, F. Ugozzoli, A. Pochini, J.-F. Dozol, C. Hill and H. Rouquette, *Angew. Chem. Int. Ed. Engl.*, 33 (1994) 1506.
- [7] A. Casnati, A. Pochini, R. Ungaro, F. Ugozzoli, F. Arnaud, S. Fanni, M.-J. Schwing, R.J.M. Egberink, F. de Jong and D.N. Reinhoudt, *J. Am. Chem. Soc.*, in press.
- [8] P.J. Dijkstra, J.A.J. Brunink, K.-E. Bugge, D.N. Reinhoudt, S. Harkema, R. Ungaro, F. Ugozzoli and E. Ghidini, *J. Am. Chem. Soc.*, 111 (1989) 7567.
- [9] R.G. Pearson, *J. Am. Chem. Soc.*, 85 (1963) 3533.
- [10] K. Kimura, H. Tamura and T. Shono, *J. Electroanal. Chem.*, 105 (1979) 335.
- [11] K.W. Fung and K.H. Wong, *J. Electroanal. Chem.*, 111 (1980) 359.

- [12] B. Rieckemann and F. Umland, *Fresenius' Z. Anal. Chem.*, 323 (1986) 241.
- [13] E.J.R. Sudhölter, P.D. van der Wal, M. Skowronska-Ptasinska, A. van den Berg, P. Bergveld and D.N. Reinhoudt, *Anal. Chim. Acta*, 230 (1990) 59.
- [14] P.D. van der Wal, M. Skowronska-Ptasinska, A. van den Berg, P. Bergveld, E.J.R. Sudhölter and D.N. Reinhoudt, *Anal. Chim. Acta*, 231 (1990) 41.
- [15] M.H. Abraham and H.C. Ling, *J. Chem. Soc., Faraday Trans. I*, 80 (1984) 3445.
- [16] P.L.H.M. Cobben, R.J.M. Egberink, J.G. Bomer, P. Bergveld and D.N. Reinhoudt, *J. Electroanal. Chem.*, 368 (1994) 193.
- [17] J.A.J. Brunink, R.J.W. Lugtenberg, Z. Brzozka, J.F.J. Engbersen and D.N. Reinhoudt, *J. Electroanal. Chem.*, 378 (1994) 185.