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Benzodipyrrole derivates as new ionophores for anion-selective electrodes: Improving potentiometric selectivity towards divalent anions

M. Cuartero[a], J.A. Ortuño[a,*], M.S. García[a], G. Sánchez[b], M. Más-Montoya[b], D. Curiel[b]

[a] *Department of Analytical Chemistry, Faculty of Chemistry, University of Murcia, 30100 Murcia, Spain*
[b] *Department of Organic Chemistry, Faculty of Chemistry, University of Murcia, 30100 Murcia, Spain*

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ABSTRACT

Two open substituted benzodipyrroles were tested as hydrogen-bond-forming anion ionophores for the development of anion-selective electrodes. These compounds were incorporated in plasticized polymeric membranes with different plasticizers, using different membrane compositions to explore their response towards several anions. The electrodes constructed with membranes containing 2-nitrophenyl octyl ether and a 0.5 molar ratio ionic additive/ionophore showed pronounced anti-Hofmeister behaviour, providing a significantly enhanced response towards the divalent anions sulfate, sulfite, thiosulfate and oxalate. The selected electrodes were also evaluated in terms of detection limits and selectivity. ^{1}H NMR experiments were carried out in an attempt to explain some aspects of the behaviour observed.

1. Introduction

Research into sensing receptors for anion recognition has intensified in recent years due to the high demand for anion sensors due to the important roles played by anionic species in chemical, biological and environmental processes in medicine, food analysis, environmental monitoring and biotechnology [1,2]. New anion-selective electrodes are continually being proposed because of the possibility of manipulating the design of molecular hosts, which are capable of selectively bind anionic guests and act as ionophores in ionophore-based membrane-selective electrodes [3–7].

The potentiometric response of ion-selective electrodes (ISEs) based on membranes containing either no ionophore or an inefficient ionophore is determined by the hydrophilicity of the tested anions and their solvation in the membrane. Anions with a high hydrophilicity give smaller responses, resulting in a response-sequence for the ISE that is reflected in the Hofmeister series [8]: perchlorate > thiocyanate > iodide ≈ salycilate > nitrate > bromide > nitrite > chloride > sulfate. In this regard, the search for sensing electrodes, based on new ionophores for determining anions that are at the very end of the Hofmeister series, has always been particularly interesting for researchers. An efficient ionophore has to modify the conventional ISE selectivity towards various anions since the transfer of specific anions from the sample solution into the membrane is enhanced by selective complexation.

Of note is the fact that the higher hydrophilicity of a given anion, the more difficult it is to construct a truly selective electrode for this anion. This partially explains why it was not until 1998 that the two first sulfate ionophores were published [9,10]. Since then, several ionophores have been reported to improve selectivity towards sulfate [11–16]. However, to our knowledge, there are few ionophores for sulfite [17–20], which is normally detected as hydrogen sulfite anion, and for oxalate [21–23], and none for thiosulfate.

Pyrrole-based structures are well established as highly effective anion hosts [24,25]. Recently, studies on the synthesis and complexation of two new open benzodipyrrole derivates (Fig. 1) have been published [26]. These compounds (I and II) revealed good affinity towards oxoanions through hydrogen bond interactions. This prompted us to evaluate their effects as anion ionophores in poly(vinyl chloride) membrane electrodes.

The goal of the present work was to test whether these ionophores significantly alter the Hofmeister series for divalent anions that are analytically important, such as sulfate, sulfite and oxalate, in order to further develop selective electrodes for their determination. In this way, the ionophores, working as hydrogen bond donors, could act as multidentate ligands with an increasing demand of the anion size and charge, as it was observed by Curiel et al. [26].

2. Experimental

2.1. Apparatus

Potentiometric measurements were recorded using a home-made high-impedance data acquisition 16-channel box connected

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* Corresponding author. Tel.: +34 868 887414; fax: +34 868 887682.
E-mail address: jortuno@um.es (J.A. Ortuño).

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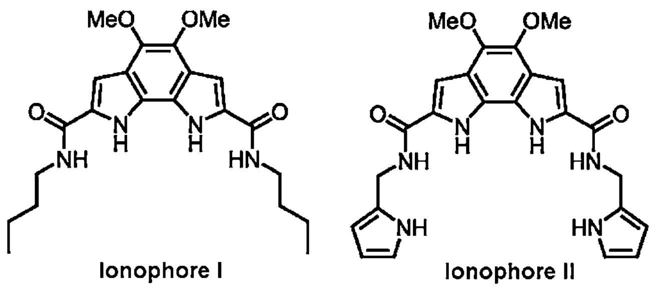

Fig. 1. Benzodipyrrole derivates used as ionophores.

to a PC by USB. An Orion Ag/AgCl double-junction reference electrode (Orion 90-02) containing 10^{-2} M KCl was also used.

^1H NMR spectra were recorded on a Bruker AV300 instrument or AV400 instrument.

2.2. Reagents and solutions

All chemicals were of analytical reagent grade and Milli-Q water was used throughout. Polyvinyl chloride (PVC) of high molecular weight, dioctyl sebacate (DOS), 2-nitrophenyl octyl ether (NPOE), 2-fluoro-2′-nitrodiphenyl ether (FNDPE), tridodecylmethylammonium chloride (TDMA-Cl) and tetrahydrofuran (THF) were purchased from Fluka. Benzodipyrroles derivatives were synthesized as depicted in literature [26]. Perchlorate, salicylate, thiocyanate, iodide, nitrate, bromide, citrate, chloride, thiosulfate, sulfate, acetate, sulfite, dihydrogen phosphate, fluoride, oxalate and hydrogen carbonate solutions were prepared by dissolving the corresponding sodium salts in water.

2.3. Membranes and electrodes

The compositions of the membranes assayed in this study are shown in Table 1. The membranes were prepared by dissolving appropriate amounts of the corresponding membrane components (PVC, plasticizer, ionophore and/or ionic additive) in 3 mL of THF. This solution was poured into a Fluka glass ring (inner diameter 28 mm, height 30 mm) on a Fluka glass plate, and allowed to settle overnight until total evaporation of THF had occurred, to obtain a thin plastic membrane. A 6-mm-diameter piece was cut out with a punch for ion-selective membranes and incorporated into a Fluka electrode body ISE containing 1×10^{-4} M KCl as an internal filling solution. The electrodes were conditioned in water until they reached a constant potential. When not in use, the electrode was kept immersed in water.

2.4. Potentiometric measurements

All potentiometric measurements were performed at room temperature. Calibrations of the electrodes were made in a dynamic way by adding, while stirring, adequate small volumes of the corresponding standard solution of anion sodium salts in 50 mL water to cover the concentration range from 1×10^{-7} to 1×10^{-2} M. The steady-state potentials were then plotted *vs.* logarithmic values of the corresponding concentrations. The values of the standard potential cell (E°) and calibration slope (S) were calculated by fitting the data within the linear portion to $E = E^\circ + S \log C_A$. Before each new calibration the electrode was conditioned in water until the primitive original potential was achieved. If the base line did not fully reach that value, the water used was renewed.

Due to the basic behaviour of SO_3^{2-}, the concentration values used in the corresponding calibration graphs were calculated from the analytical concentrations and the SO_3^{2-} base dissociation constants [27].

2.5. ^1H NMR experiments

Titration experiments: A stock solution of the corresponding ionophore was prepared in the appropriate deuterated solvent. The titrant species (ionic additive and/or plasticizer) were then dissolved in the corresponding volume of the former solvent to obtain the correct concentration of titrant. Aliquots of the latter solution were added to the solution which contained the ionophore and no dilution effects were considered. Chemical shifts were referred to the solvent residual peak. Binding constants were calculated with an error of less than 15%.

3. Results and discussion

The potentiometric responses of the electrodes built with plasticized polymeric membranes containing ionophores I and II (Fig. 1) towards perchlorate, salicylate, thiocyanate, iodide, nitrate, bromide, citrate, chloride, thiosulfate, sulfate, acetate, sulfite, dihydrogen phosphate, fluoride, oxalate and hydrogen carbonate were evaluated.

Usually, a relatively high concentrated of primary ion solution is used in the composition of the internal filling solution [28]. How-

Table 1
Membrane compositions assayed.

Membrane	Components							
	PVC	DOS	NPOE	FNDPE	Ionophore I	Ionophore II	TDMACl	
							wt%	mol ratio[a]
A	33		66				1	
B	32.8		65.6		0.6		1	0.5
C	32.6		65.3			1.1	1	0.5
D	32.8	65.6			0.6		1	0.5
E	32.6	65.3				1.1	1	0.5
F	32.8			65.6	0.6		1	0.5
G	32.6			65.3		1.1	1	0.5
H	33		66		0.6			
I	33		66			1.1		
J	33		65		1		1	0.7
K	33		64.9		1		0.4	0.3
L	33		64.2			1	1	0.8
M	33		65.2			1	0.5	0.3

[a] mol ratio relative to ionophore.

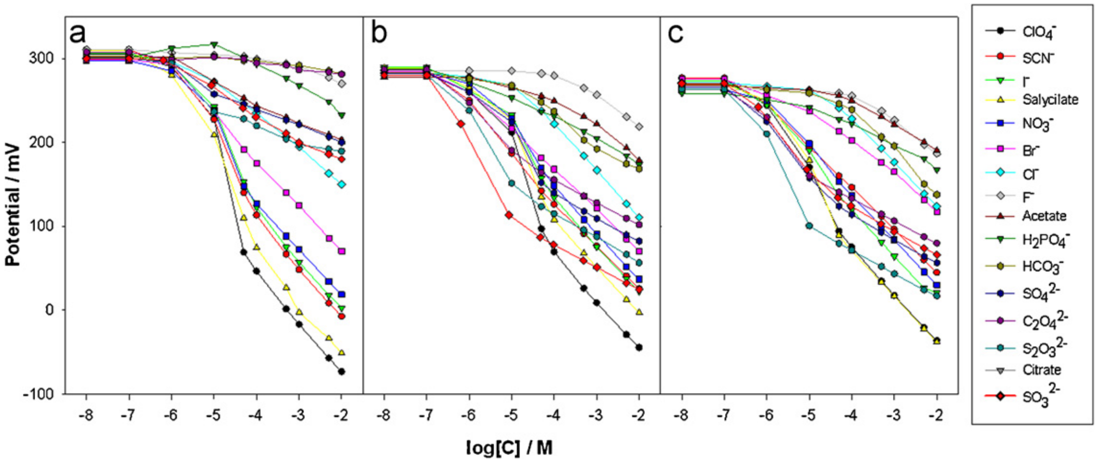

Fig. 2. Calibration graphs obtained with ISEs constructed with the blank membrane (a), with membrane B containing ionophore I (b) and with membrane C containing ionophore II (c).

ever, recent findings have shown that this procedure has adversely affects the detection limit due to the flux of the primary ion from the inner solution to the sample solution [29]. This flux competes at the membrane/solution interface with the primary ion arising from the bulk of the sample. For this reason, a relatively diluted internal filling solution, 10^{-4} M, of potassium chloride was used. The calibrations of the different anions assayed were made in water in order to avoid the contribution of any other anion to the membrane potential [30].

Under these conditions, the responses of the electrodes constructed with NPOE plasticized membranes, containing only TDMA-Cl as anion exchanger (membrane A of Table 1, also named blank membrane) and, in addition, the ionophores I or II (membranes B and C of Table 1), towards all the anions assayed are shown in Fig. 2. As can be seen, the presence of the ionophores strongly influenced the response of the corresponding electrode. From a comparison of the response of the three membranes towards the different anions it can be concluded that, while the blank membrane showed an expected Hofmeister response profile, the membranes containing ionophores displayed significant alterations in this order. This behaviour mainly affected the divalent anions assayed, whose responses were drastically improved with regard to monovalent anions. The calibration graphs for many anions exhibited a super-Nernstian portion in the response. This is an expected response [31,32] for anions preferred by the membrane when a discriminated anion is initially present in the membrane, and that has been successfully exploited for the determination of polyions [33–36].

3.1. Influence of the plasticizer

The effect of the membrane plasticizer on the potentiometric responses towards the different anions was examined using three plasticizers with different dielectric constants. In addition to NPOE ($\varepsilon = 24$), two other plasticizers were also used: DOS with a lower dielectric constant ($\varepsilon = 4$) and FNDPE with a higher dielectric constant ($\varepsilon = 50$). The corresponding calibration graphs of the electrodes containing membranes D–G constructed with the last two plasticizers and ionophores I and II (see Table 1) are shown in Fig. 3. From these results and those shown in Fig. 2, it can be seen that the membranes constructed with DOS (Fig. 3a and b) and FNDPE (Fig. 3c and d) exhibited poorer responses than that constructed with NPOE (Fig. 2b and c) for all the anions tested. It was also observed that the response of the membrane plasticized with FNDPE decreased in successive calibrations, as shown in Fig. 3c and d.

The lower response displayed by membrane containing DOS is in agreement with previously reported results based on hydrogen-bonding ionophores, which found that the transfer of the anion from the sample to the membrane phase is facilitated by a higher polarity plasticizer in the membrane [37,30,7]. The weaker response detected for FNDPE, with a higher dielectric constant, led us to further study its behaviour by means of ^{1}H NMR experiments. The aim of this study was to gain insight into any possible interference on the part of the plasticizer in the anion binding ability of the ionophore. Therefore, ^{1}H NMR spectra were recorded for both ionophores I and II individually and in the presence of FNDPE. Experiments were carried out in deuterated tetrahydrofu-

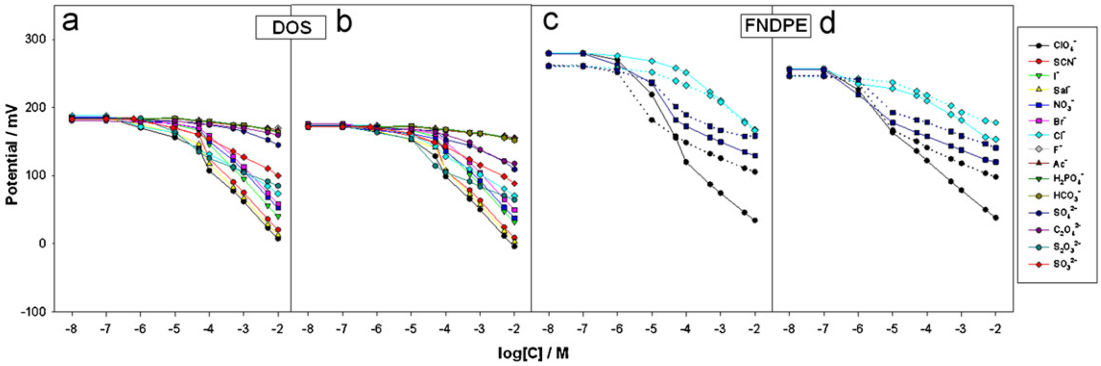

Fig. 3. Calibration graphs obtained with membranes containing DOS and ionophores I (a) and II (b), membranes D and E, respectively, and containing FNDPE and ionophores I (c) and II (d), membranes F and G, respectively. In the case of FNDPE dotted lines indicate that calibration graphs were made after three days.

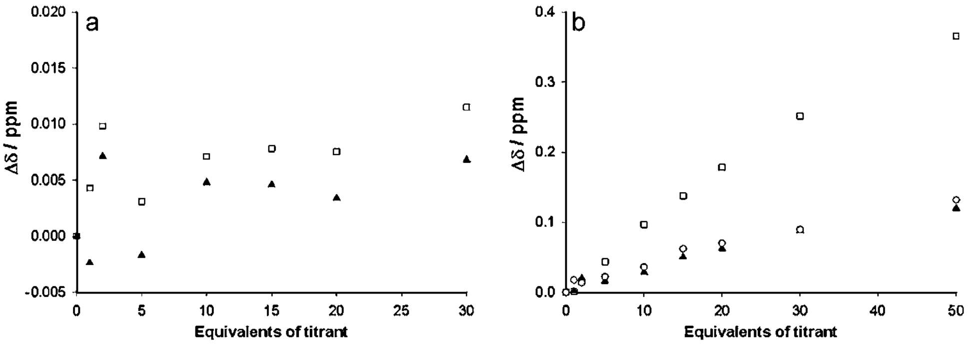

Fig. 4. Evolution of the ^{1}H NMR chemical shift recorded for the peaks of ionophore II corresponding to (□) NH-benzodipyrrole, (▲) NH-amide and (○) NH-appended pyrrole, upon titration with (a) FNDPE and (b) FNDPE-TDMACl. [ionophore] = 2×10^{-3} M in THF-d_8.

ran to achieve a balance between the solubility of the ionophore and the non-competitive nature of the solvent. These conditions were intended to favour any possible non-covalent interaction between the ionophores and the guest species and to approximate the conditions found in the membrane. These studies revealed that the peaks assigned to the benzodipyrrole/amide NH protons did not undergo any shift when FNDPE was added. Therefore, it could be concluded that, under our experimental conditions, there was no interaction between the ionophores and FNDPE.

Conversely when the titration was carried out with a mixture of FNDPE and the ionic additive TDMACl, the latter in a ratio of 1 mol% relative to the ionophore, a downfield shift of the NH protons in the ionophore was detected. The fact that all three protons (NH-benzodipyrrole, NH-amide and NH-pyrrole) simultaneously are displaced in the ^{1}H NMR spectra of the ionophore confirmed that three different hydrogen bonds intervene in the anion complexation.

As an example, the results obtained with ionophore II are collected in Fig. 4. Taking all these experiments into account, it can be concluded that the negative effect of FNDPE is not due to it competing with the anion of the sample in the complexation process by the ionophore in the membrane.

Although FNDPE was used in some ISEs reported by Katsu et al. [38], the particular behaviour of this plasticizer has been already observed [39,40] although not totally explained. For membranes plasticized with low and medium dielectric constant solvents, like DOS and NPOE, salt extraction is efficiently suppressed by adding ionic sites in the membrane. However, to our knowledge, this phenomenon has not been checked for the much more polar plasticizer FNDPE. Due to its high dielectric constant, FNDPE is more susceptible to experience permselectivity breakdowns (Donnan Failure). Interestingly, another interesting observation was that made concerning the high water uptake by FNDPE plasticized membranes [39]. It was found that the penetration of water within the membrane produces a thin external region with a high water content [41] that affects the response of the electrode.

On the basis of the results obtained, NPOE was used as the membrane plasticizer for all further experiments.

3.2. Influence of ionic additive

The effect of the incorporation of an ionic lipophilic additive to the membranes was evaluated by studying the potentiometric response of membranes containing PVC, NPOE and the corresponding ionophore, with (membranes B and C, Table 1) and without (membranes H and I, Table 1) ionic additive. The membranes without ionic additive showed a practically negligible response for all the anions assayed, while those containing the additive showed a Nernstian response portion for most anions assayed, as is shown in Fig. 2b and c. As is well known, the presence of lipophilic ionic sites with a charge sign opposite to that of the primary ions is decisive for obtaining a good response of ionophore-based ISEs [42].

The influence of the additive/ionophore molar ratio in the membrane composition (see Table 1) in the response to the different anions was also studied. As the ratio increased from 0.3 to 0.5, the response of the membranes containing either ionophore increased for all the anions assayed, while the anti-Hofmeister behaviour remained. However, when this ratio was further increased to *ca.* 0.7, the anti-Hofmeister response achieved for the divalent anions decreased, since the response was close to that obtained for the membrane containing only the ionic additive.

According to these results, membranes B and C, containing ionophores I and II, NPOE and a 0.5 additive/ionophore molar ratio, were selected for further studies.

3.3. Detection limits

As mentioned above, the response of the selected membranes towards many anions displayed a super-Nernstian response portion. Two criteria were proposed and recommended by IUPAC to calculate the detection limit for this type of response [43,44]. Both criteria involved the transposition of the rules used to calculate the detection limit for ISEs with conventional response to ISEs with a super-Nernstian response portion. One of them, considered as an “attainable” detection limit, is obtained from the cross-section of the two linear parts of the response function, i.e. the extrapolated lines of the Nernstian and nonresponsive segments of the ISE response curve [43]. Although the practical value of this criterion has been questioned, we have used it to complement the other criterion shown below which is rather demanding.

As regards the second criterion, named extended definition, the detection limit is calculated from the measured potential which derivates $S \times \log 2$ from the extrapolated Nernstian response [44,31]. The detection limit values obtained for the selected membranes containing ionophores I and II, together with those for the blank membrane, following both criteria, are collected in Table 2. As can be seen, the “attainable” detection limits obtained were much lower than those obtained with the extended definition. For sulfate, oxalate, thiosulfate and sulfite, the detection limits for the membranes containing either of the ionophores were lower than that obtained for the blank membrane. This effect is more pronounced so far as the “attainable” detection limits are concerned. The improvement to more than four concentration decades in the case of oxalate is of particular note.

3.4. Selectivity

Selectivity is the most important characteristic of ISEs since this parameter provides information on the ability of the sensing

Table 2
Detection limits calculated for ISEs constructed with membranes containing ionophore I (membrane B), ionophore II (membrane B) and the blank membrane (membrane A).

Anions	LD ionophore I (M)		LD ionophore II (M)		LD blank membrane (M)	
	Attainable	Extended	Attainable	Extended	Attainable	Extended
ClO_4^-	3.8×10^{-7}	7.9×10^{-6}	1.3×10^{-7}	9.9×10^{-6}	2.8×10^{-7}	2.5×10^{-7}
SCN^-	1.0×10^{-7}	8.5×10^{-6}	2.3×10^{-7}	1.9×10^{-5}	3.5×10^{-7}	4.4×10^{-7}
I^-	7.2×10^{-7}	9.3×10^{-6}	2.2×10^{-7}	1.2×10^{-5}	6.4×10^{-7}	4.6×10^{-6}
Sal^-	5.5×10^{-7}	8.8×10^{-6}	1.8×10^{-7}	5.9×10^{-4}	2.4×10^{-7}	4.7×10^{-7}
NO_3^-	8.8×10^{-7}	2.2×10^{-5}	5.9×10^{-7}	2.5×10^{-5}	5.3×10^{-7}	3.7×10^{-6}
Br^-	3.9×10^{-7}	6.8×10^{-5}	1.4×10^{-6}	1.2×10^{-4}	6.2×10^{-7}	4.8×10^{-6}
Cl^-	6.4×10^{-6}	3.4×10^{-4}	9.9×10^{-6}	4.0×10^{-4}	2.4×10^{-6}	1.3×10^{-4}
F^-	3.0×10^{-5}	2.8×10^{-5}	3.0×10^{-5}	1.3×10^{-4}	8.4×10^{-6}	3.1×10^{-3}
Ac^-	7.4×10^{-6}	4.4×10^{-4}	1.3×10^{-5}	1.3×10^{-4}	3.7×10^{-7}	8.2×10^{-5}
$H_2PO_4^-$	6.3×10^{-7}	5.5×10^{-3}	2.6×10^{-6}	2.0×10^{-4}	5.0×10^{-5}	4.9×10^{-5}
HCO_3^-	3.9×10^{-6}	4.8×10^{-5}	1.2×10^{-5}	6.5×10^{-5}	1.2×10^{-5}	1.3×10^{-3}
SO_4^{2-}	9.5×10^{-8}	7.0×10^{-6}	2.7×10^{-9}	9.0×10^{-6}	6.7×10^{-8}	3.0×10^{-5}
$C_2O_4^{2-}$	3.7×10^{-12}	6.7×10^{-6}	1.3×10^{-9}	6.2×10^{-6}	2.1×10^{-6}	8.8×10^{-4}
$S_2O_3^{2-}$	4.4×10^{-10}	7.5×10^{-6}	1.3×10^{-11}	8.0×10^{-6}	1.5×10^{-9}	6.1×10^{-5}
SO_3^{2-}	1.2×10^{-11}	6.5×10^{-6}	1.1×10^{-9}	9.5×10^{-6}	5.0×10^{-7}	3.4×10^{-5}

membrane to discriminate the primary ion from other ions of the same charge sign. The separate solution method (SSM) was used here to determine the selectivity coefficients of the ISEs containing ionophores I and II. Unbuffered solutions were used in these studies to avoid any contribution from the buffer anions [30]. The values for the ISE containing the blank membrane were also obtained for comparison purposes.

Following the recommendations of Bakker et al. [45] to avoid biased values, no selectivity coefficients were calculated for interfering anions which did not show a Nernstian portion in the calibration graph. Instead, the calibration graphs for these anions can be examined (Fig. 2b and c).

The logarithmic selectivity coefficient values referred to chloride anion and the differences between the values obtained for each ionophore and the blank membrane are shown in Fig. 5. As can be seen in Fig. 5b, the presence of either ionophore in the membrane decreased the selectivity coefficients of all monovalent anions. This decrease was about 300 and 600 times in the case of the selectivity coefficients for perchlorate and salycilate, respectively, using ionophore I. In addition, the selectivity coefficients considerably increased for all the divalent anions, of note being the increase of more than 10,000 times for oxalate, when using ionophore II. Taking both effects together, the selectivity for divalent anions with respect to monovalent anions increased drastically. A careful comparison between the effects of both ionophores showed that the choice of either ionophore depended on each I, J pair considered. Thus, for I = chloride and J = sulfite the ionophore I is more convenient, while for J = oxalate the ionophore II is better.

The good results obtained for the oxalate anion were further supported by ^1H NMR experiments. When each ionophore was titrated with oxalate anion (in the form of tetrabutylammonium salt, TBA_2oxalate) in acetone-d_6 solution, a noticeable difference could be observed in the titration isotherms (Fig. 6). Ionophore II clearly brought about the saturation of the complexation equilibrium at a lower anion concentration, which indicates a higher stability of the complex.

This is quantitatively supported by the binding constant of the association equilibrium. The analysis of the experimental data by non-linear curve fitting to a 1:1 stoichiometry model resulted in an association constant value of 1.6×10^4 for ionophore II. Due to

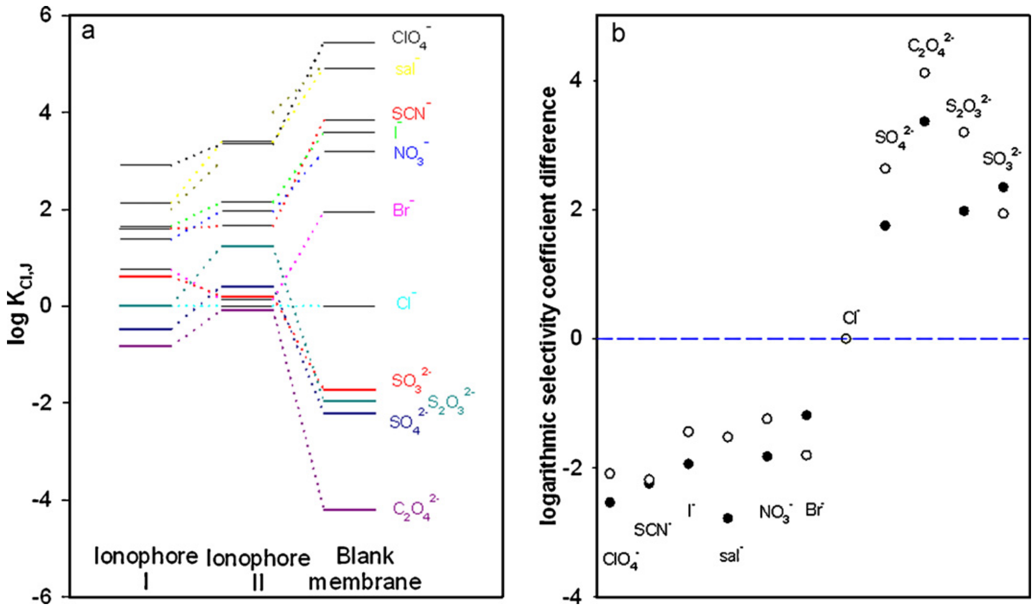

Fig. 5. (a) Selectivitiy coefficients calculated for membranes constructed with ionophores I and II (membranes B and C respectively) and for the blank membrane (membrane A). (b) Difference between the logarithmic selectivity coefficients of membrane with ionophore I and the blank membrane (●) and of the membrane with ionophore II and the blank membrane (○).

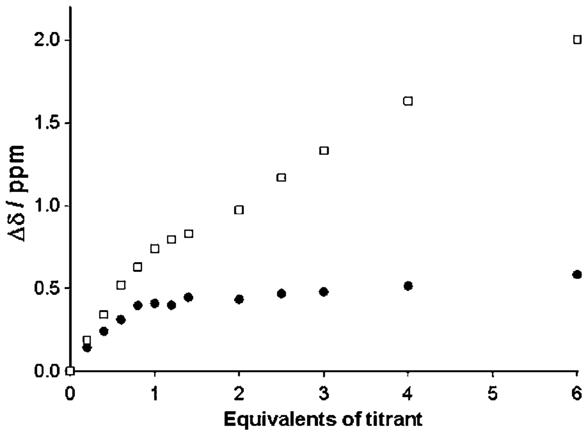

Fig. 6. Evolution of the ^{1}H NMR chemical shift recorded for the NH-amide peaks of ionophore II (●) and ionophore I (□) upon titration with TBA_2oxalate. [ionophore] = 2 × 10^{-3} M in acetone-d_6. [oxalate] = 0.08 M.

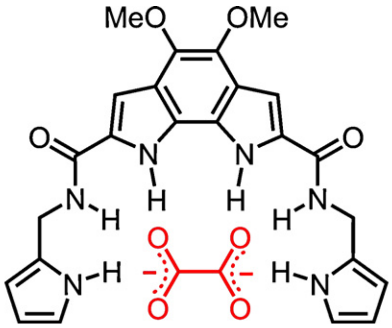

Fig. 7. Proposed binding mode for the complex of the divalent anion oxalate with ionophore.

the weak interaction established between ionophore I and oxalate anion, the experimental data were not adequate enough for an accurate calculation of the binding constant. Anyhow, a value in the range 50–70 could be estimated. The higher constant found with ionophore II explains the higher selectivity coefficient achieved with this ionophore.

We can conclude that the presence of up to six hydrogen bond donor groups and the good cavity size correspondence brings about a remarkable enhancement in the complexation of oxalate anion by ionophore II (see proposed structure in Fig. 7) compared with the results obtained for ionophore I.

4. Conclusions

The introduction of a benzodipyrrol in plasticized polymeric membranes lead to a considerable improvement in potentiometric selectivity for the divalent anions sulfate, sulfite, oxalate and thiosulfate. The benzodipyrrol substituents influence the anion selectivity profile. ^{1}H NMR studies explained the good results obtained for oxalate and ionophore II. The results here obtained can be exploited for the tailor made development of ion-selective electrodes for a particular divalent anion.

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