

Influence of decyl alcohol on the potentiometric behavior of three *p*-alkylbenzenesulfonate ion-selective electrodes

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Abstract

The influence of decyl alcohol on the potentiometric response of three *para*-alkylbenzenesulfonate (*p*-RBS) electrodes is analyzed. The results are clearly dependent on the membrane surface polarity due to the presence of the alcohol. The ionophore was the complex trioctylmethylammonium-*p*-RBS, (TOMA⁺)-*p*-RBS⁻, with R = H, CH₃, and C₂H₅. The nature of the complex plays a fundamental role on the potentiometric behavior of the electrode showing that the more hydrophobic the complex, the better the potentiometric responses. Moreover, the electrodes selectivities for several hydrophilic and hydrophobic interfering anions were determined. The potentiometric results with interfering anions were coherent with the Pearson's hard and soft acid–base character of these anions.

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1. Introduction

The use of ion-selective electrodes (ISEs) is a relatively rapid, widely employed technique useful to determine the analytical concentrations of a myriad of ions. An exhaustive review has been published by Buhlmann [1]. In a previous paper [2], we reported that membrane polarity seems to play a fundamental role in the potentiometric response of a xanthate ISE. In fact, the addition of an amount of dodecyl alcohol as low as 3 μmol to a plastic liquid membrane yields Nernstian responses no matters what plasticizer is used.

In another work [3] we have reported that phenols affect the potentiometric response of a nitrate ISE in such a way that phenols that contain electron-withdrawing substituents induce sub-Nernstian slopes. On the other hand, those phenols containing electron-releasing substituents produce Nernstian responses. The results were explained assuming that nitrate dissociation is mediated by the strength

of the cation–π interaction between the phenol and the ammonium polar group acting as counterion.

Among the more important sulfonate-type ISE are those related to sulfonate detergents, due to their enormous industrial relevance. In fact, an electrode for linear dodecylbenzene sulfonate, DBS, doped with polypyrrole has been developed [4] by anodic polymerization of pyrrole in the presence of DBS. This PVC electrode showed a nearly Nernstian response when *ortho*-nitrophenyloctylether was used as plasticizer and hyamine as additive. The effect of alkylphenols on the potentiometric behavior of organic sulfonate ions has been studied [5]. The main feature was that the electrode selectivity increases with the presence of phenol which probably interacts by hydrogen bonding with sulfonate. Electron impact mass spectrometry has been also used to distinguish sodium alkylbenzene sulfonate isomers as well as to determine the presence of homologs [6].

The equilibrium concentration of free organic counterions is a crucial aspect in binding studies related to their interaction with micelles, polyelectrolytes, colloidal solutions, etc. These studies can be easily performed by using

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ISEs; consequently, in the present work three PVC sulfonate electrodes are constructed using the complex trioctylmethylammonium-*p*-alkylbenzenesulfonate, $\text{TOMA}^+ - p\text{-RC}_6\text{H}_5\text{-SO}_3^-$, with $\text{R} = \text{H}, \text{CH}_3,$ and C_2H_5 . The effect of decyl alcohol on their potentiometric response is analyzed.

2. Materials and methods

Trioctylmethylammonium chloride (TOMA^+Cl^-), dioctylphthalate (DOP), dichloromethane, 1-decanol, tetrahydrofuran, and polyvinyl chloride (PVC), with an average molecular weight of 233,000 were all from Aldrich, Milwaukee, WI, USA. Sodium benzene sulfonate, sodium 4-methylbenzene sulfonate, and 4-ethylbenzene sulfonic acid were also from Aldrich and of the highest purity grade available. The acid was previously neutralized with aqueous NaOH and recrystallized several times from acetone before using.

The complex $\text{TOMA}^+ - p\text{-RBS}^-$ with $\text{R} = \text{H}, \text{CH}_3,$ or C_2H_5 was prepared by dissolving TOMA^+Cl^- in dichloromethane and an equimolar amount of the *p*-RBS sodium salts in water. These solutions were poured in a decanter funnel and mixed vigorously, and then the organic phase was washed several times with water until chloride anion was not detected in the aqueous phase. The phases were separated and the organic phase containing the complex was dried with anhydrous MgSO_4 . The $\text{TOMA}^+ - p\text{-RBS}^-$ complex was obtained by solvent distillation under reduced pressure.

All membranes were constructed by dissolving 10 mg of the $\text{TOMA}^+ - p\text{-RBS}^-$ complexes, 1.14 g of DOP, and 0.35 g of PVC in 20 ml of THF. In some cases, 3 μmol of 1-decanol were added from a stock 1-decanol solution in THF. These mixtures were gently heated until the total volume had been reduced to approximately 8 ml. Then these solutions were poured into a 10-cm-diameter Petri dish and were left to slowly evaporate the solvent overnight.

A disc of approximately 1 cm in diameter was fixed on the base of a PVC tube with a PVC/THF paste. The tube was partially filled with 5×10^{-3} M of *p*-RBSNa and 5×10^{-3} M KCl as inner solution. The inner reference electrode was Ag/AgCl and the outer reference electrode was a double-junction Ag/AgCl Orion electrode. The cell was the following:

$\text{Ag/AgCl} \mid \text{inner filling solution} \parallel p\text{-RBSNa}_{(\text{aq})} \mid \text{Ag/AgCl}$.

All the measurements were performed at $25 \pm 0.1^\circ\text{C}$ with a Corning Model 12 Research potentiometer and they were highly reproducible. The potentiometric responses were very rapid, between 1 and 5 s, and also very stable, independent of whether the membrane contained the doping agent or not. In all cases, to evaluate the selectivity coefficients, the method of fixed interference [7] was used. They were determined with 0.001 M of added interfering salts.

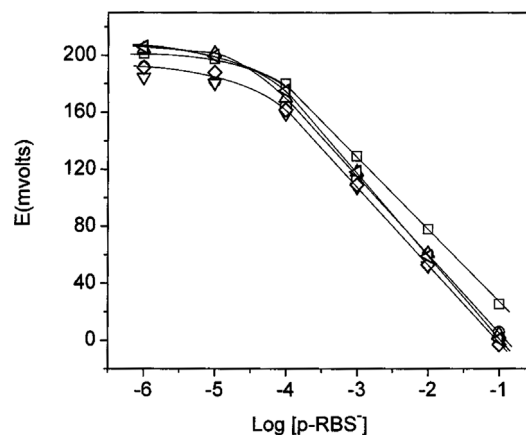


Fig. 1. Calibration curves of *p*-RBS electrodes. Without 1-decanol: (□) BS; (○) *p*-MeBS; (△) *p*-EtBS, with 3 μmol of 1-decanol per membrane: (▽) BS; (◇) *p*-MeBS; (◁) *p*-EtBS.

3. Results and discussion

Fig. 1 shows the potentiometric responses of electrodes constructed as explained above. In all cases the behavior is nearly linear until 10^{-3} – 10^{-4} M *p*-RBS. The slopes of the linear parts of these plots are summarized in Table 1. As can be seen in all cases, the slopes increase as the *para* group size increases. The complex $\text{TOMA}^+ - \text{BS}^-$ is the most hydrophilic complex, as compared with *p*-MeBS and *p*-EtBS. It shows the highest impediment to reaching the membrane surface, in contact with the aqueous phase. On the other hand, the presence of 1-decanol modifies the membrane surface polarity by extending its OH groups to the water phase while generating a hydrophobic barrier with its aliphatic tails, perpendicular to the membrane surface. Apparently, this apolar barrier can be more easily crossed by $\text{TOMA}^+ - p\text{-EtBS}^-$, the more hydrophobic complex. A similar effect of 1-dodecanol was reported in an isopropyl xanthate electrode [2]. These results support the hypothesis that the membrane surface polarity seems to play an important role in the potentiometric behavior, perhaps as relevant as the membrane fluidity.

Since the *p*-EtBS electrode with 1-decanol as additive had the best potentiometric response, the interference study was performed with this type of electrode. Figs. 2 and 3 show the behavior of the potentiometric responses as a function of the $\log[p\text{-EtBS}^-]$ for several hydrophilic and hydrophobic interfering anions, respectively. From similar plots as those of Figs. 2 and 3, the selectivity constants, K_{ij} , were also determined with electrodes in absence of 1-decanol in their membranes. In Table 2 are summarized the K_{ij} values, in the presence and absence of decyl alcohol, respectively. Values in Table 2 show that the *p*-EtBS electrode has higher selectivity to *p*-EtBS than all the other hydrophilic and hydrophobic interfering anions. The only exception is *p*-MeBS, whose K_{ij} approaches to one. On the other hand, hydrophilic anions such as nitrate, chloride and sulfate behave like interfering agents following the order:

Table 1
Effect of 1-decanol on $d(E)/d(\log[p\text{-RBS}])$

Electrode	$\text{TOMA}^+-\text{BS}^-$	$\text{TOMA}^+-p\text{-MeBS}^-$	$\text{TOMA}^+-p\text{-EtBS}^-$
Without 1-decanol	-51.40	-52.85	-55.35
With 1-decanol	-53.65	-54.95	-58.40

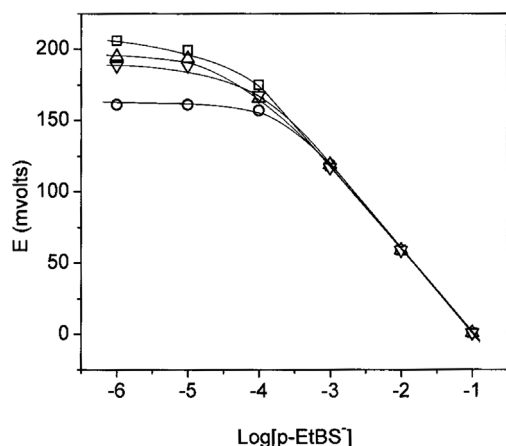


Fig. 2. Calibration curves for $p\text{-EtBS}$ electrode with $3\ \mu\text{mol}$ of 1-decanol per membrane in the presence of $0.001\ \text{M}$ of interfering anions: (○) nitrate, (Δ) sulfate, (∇) chloride, and (□) without interfering anion.

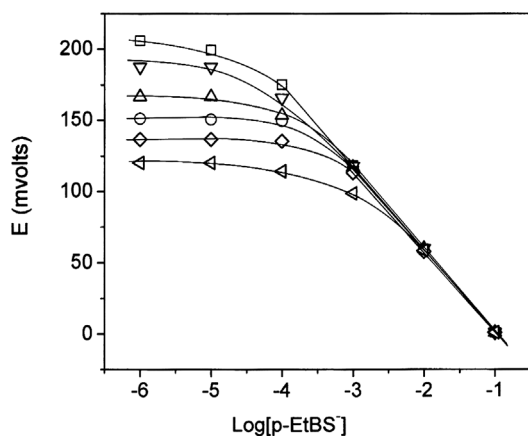


Fig. 3. Calibration curves for $p\text{-EtBS}$ electrode with $3\ \mu\text{mol}$ of 1-decanol per membrane in the presence of $0.001\ \text{M}$ of interfering anions: (○) acetate, (Δ) benzoate, (∇) oxalate, (◇) BS, (◁) $p\text{-MeBS}$, and (□) without interfering anion.

nitrate > chloride > sulfate, if the membrane does not contain decyl alcohol. These anions are Pearson's hard bases, whose strength is precisely the inverse of their interfering capacity. The ammonium group is a hard acid, but TOMA^+ can be considered borderline or almost a soft acid due to the large size of its aliphatic substituents. Sulfonate groups can be considered as soft bases when they are linked to a *para*-alkylbenzene group, then their ability to bind TOMA^+ is greater than that which occurs with the above hydrophilic cations. Therefore, the interfering order can be explained in terms of the base strength of the anions. Nitrate is softer than sulfate, and then it competes with sulfate for TOMA^+ more successfully. Obviously, chloride is an intermediate case. On

Table 2
Selectivity constants of interfering anions for $p\text{-EtBS}$ electrode

Interfering anion	Without 1-decanol	With 1-decanol
Nitrate	0.170	0.176
Chloride	0.120	0.028
Sulfate	0.054	0.015
Oxalate	0.017	0.060
Benzoate	0.018	0.141
Acetate	0.222	0.264
Benzene sulfonate	0.361	0.474
Methylbenzene sulfonate	0.936	0.922

the other hand, without 1-decanol, the situation seems to be the inverse at least in the case of chloride and sulfate. These anions having a hydrophilic character, the transport of their complexes with TOMA^+ through the hydrophobic barrier formed only by the plasticizer molecules at the surface, is easier than if only 1-decanol molecules were present. In fact, these molecules should be packed at the interface in a similar way to alcohol molecules; with their polar groups pointing to the water phase and their apolar groups entering into the membrane. However, structurally 1-decanol can produce a more ordered interface structure than DOP molecules.

On the other hand, the behavior of the hydrophobic anions is clarifying. In fact, oxalate, acetate, and benzoate are hard bases. Their respective interactions with TOMA^+ are less favorable than that of $p\text{-EtBS}^-$ with TOMA^+ and their interfering capacity follows the order oxalate < benzoate < acetate, if no alcohol is present. However, in presence of 1-decanol the interfering order is the inverse. Thus, the TOMA^+ complex with these hydrophobic anions can cross the above mentioned hydrophobic barrier more easily than hydrophilic TOMA^+ complexes.

The interfering abilities of BS^- and $p\text{-MeBS}^-$ are obviously due to their soft base character consistent with the soft acid character of TOMA^+ and for this reason their higher values of K_{ij} as compared with those of hydrophilic anions. However, there is an additional effect due to the greater hydrophobic character of $p\text{-MeBS}^-$ as compared with that of BS^- . In fact, the former interacts to a larger extent than BS^- with cationic quaternary ammonium type head groups [8]. For this reason $p\text{-MeBS}^-$ is a better interfering agent than BS^- .

From the above results it can be concluded that the polarity of membrane surface plays a fundamental role on the potentiometric responses of this type of electrodes.

The 1-decanol molecules near the membrane surface probably adopt an orientation such that their polar OH groups point to the water phase and the aliphatic tails form

an inner apolar layer perpendicular to the surface. Apparently, this shell can be traversed more easily by the more hydrophobic complexes. In the case of hydrophilic anions, the membrane selectivity improves by the addition of 1-decanol whereas in the case hydrophobic anions, the selectivity decreases. This behavior can be explained in terms of the acid–base strength of the interaction between TOMA^+ and $p\text{-RBS}^-$ and also on the hydrophilic–hydrophobic character of the resulting complexes.

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