Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Colloid and Interface Science 295 (2006) 155–158

JOURNAL OF
Colloid and
Interface Science

www.elsevier.com/locate/jcis

Potentiometric behavior of ion-selective electrodes to large cationic species modulated by decyl alcohol

Walton J. Cabrera [a], Marianne A. Kaempfe [a], Marcela D. Urzúa [b], Hernán E. Ríos [b,*]

[a] *Departamento de Química, Universidad Arturo Prat, Casilla 121, Iquique, Chile*
[b] *Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653, Correo Central, Santiago, Chile*

Received 19 May 2005; accepted 27 July 2005

Abstract

The effect of 1-decanol on the potentiometric response of three ion-selective electrodes to large cationic species is analyzed. The electrodes were constructed with plasticized PVC membranes. The results suggest that 1-decanol alters the ionic transport through the membrane/water interface to an extent that depends on the strength of the active ion pair. The water solubility of the cation, its molecular weight, and the size of the ion pair seem to be relevant factors in this type of behavior. The potentiometric selectivity coefficients are also dependent on the presence of 1-decanol in the membrane. These results are similar to those already described in ion-selective electrodes with membranes capable of sensing anionic benzene sulfonate-type systems. Thus, the effect of the alcohol appears to be general by affecting mainly the membrane surface polarity.

Keywords: Ion-selective electrodes; Papaverine; Procaine; Lidocaine; 1-Decanol; Doping agent

1. Introduction

In the past 15 years interest in quantifying drugs in biological fluids in a rapid and reliable way has increased substantially. The main efforts have been focused on detecting illicit drugs due to the enormous social consequences associated with their consumption [1–9]. However, the instrumentation available is very expensive and the acquisition of data is very slow [10–12]. Consequently, many efforts have been dedicated to obtaining alternative sensors as tools to solve this analytical problem.

The molecules investigated in the present work are very important in medicine, their concentration being a crucial aspect in biological media. In fact, the medical application of these active principles requires careful supervision of this variable. Ion-selective electrodes, ISE, appear as attractive devices for sensing drugs. On the other hand, in recent works the influence of doping agents such as aliphatic alcohols [13,14] and phenols [15] on the potentiometric behavior of ISE has been reported. The working hypothesis was that membrane surface polarity plays an important role, perhaps as relevant as membrane fluidity, and the reported results were consistent with the above hypothesis. However, these works were mainly focused on ISE that were able to detect anions, e.g., xanthates [13], nitrates [14], and several *p*-alkylbenzene sulfonates [15]. The aim of the present article is to test whether this effect is present in ISE that are able to detect large cations, particularly those electrodes that have been developed to detect drugs [16].

Therefore, in the present work the effect of 1-decanol on the potentiometric responses of three ion-selective electrodes [16] for sensing cations is studied. These cations were derived from drugs that contain at least one nitrogen atom, from which it is possible to obtain the respective ammonium salts. Specifically, the tetraphenylborate complexes of procaine, papaverine, and lidocaine, $TPB^-–RN^+H$, were synthesized to construct the individual PVC membrane electrodes.

---

[*] Corresponding author.
E-mail address: hrios@uchile.cl (H.E. Ríos).

0021-9797/$ – see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2005.07.061

2. Materials and methods

2.1. Synthesis of the complexes tetraphenylborate$^-$–RN$^+$H with RN = procaine, papaverine, or lidocaine

One gram of sodium tetraphenylborate, TPB$^-$, was dissolved in 50 ml of an HCl solution at pH 3. Another equivalent molar amount of the drug, RN, was dissolved in 20 ml of the same aqueous HCl solution at pH 3 in order to obtain the respective ammonium salts, RNH$^+$Cl$^-$. Both solutions were mixed under constant agitation to obtain a white precipitate corresponding to the complexes TPB$^-$–RN$^+$H. The solids were filtered and washed with distilled water to eliminate the excess of ionic species. Then these solids were dried under reduced pressure at 40 °C overnight. The crystals obtained were dissolved in acetone and the solutions dried with anhydrous $MgSO_4$, these solutions were then filtered, and the acetone was eliminated by rotovaporation and the solids dried under reduced pressure until constant weight. Kulapina and Barinova [16] reported a 1:1 stoichiometric relationship for this type of complex between TPB$^-$ and RN$^+$H. A thin-layer chromatographic analysis showed only one product corresponding to the complexes TPB$^-$–RN$^+$H.

2.2. Membrane construction of RN$^+$H, the ammonium salts of procaine (Pro$^+$), papaverine (Pap$^+$), and lidocaine (Lido$^+$)

The membranes were prepared by dissolving 0.35 g of poly(vinyl chloride), PVC, with 1.14 g of di(2-ethylhexylphthalate) (DOP) and 0.01 g of the complex TPB$^-$–RN$^+$H in 20 ml of THF. As will be indicated, in some cases, the membranes contained 3 μmol/membrane of 1-decanol. These solutions were poured into 10 cm Petri dishes and the solvent was slowly and exhaustively evaporated.

2.3. Construction of the RN$^+$H electrodes

A small portion of the membrane was glued with a PVC/THF paste to the end of a PVC tube. The tube was then filled with an aqueous solution containing 5×10^{-3} M KCl and 5×10^{-3} M RN·HCl. An Ag/AgCl electrode was used as internal reference, whereas a double-junction Orion calomel electrode was used as outer reference electrode. The following diagram shows the cell used in the present work:

Ag/AgCl|KCl 0.005 M, RN·HCl 0.005 M ||
RN·HCl (aq)|KCl satd.|calomel.

All the measurements were performed at 25 ± 0.1 °C with a Corning Research Model 12 potentiometer. All the electrodes were tested 60 days after their first use and their responses were highly reproducible.

Tetraphenyl sodium borate (TPBNa), di(2-ethylhexylphthalate) (DOP), poly(vinyl chloride) (PVC), with an average molecular weight of 233,000, and procaine, lidocaine, and papaverine hydrochlorides were all from Aldrich, Milwaukee, WI of the highest purity available. All other reagents used were analytical grade. In order to evaluate the potentiometric selectivity coefficients, the method of fixed interference was used.

3. Results and discussion

Fig. 1 shows the potentiometric behavior of the electrodes for the different cations where the membranes were constructed in the presence and absence of 1-decanol, using DOP as plasticizer and the ion pairs TPB$^-$–RN$^+$H as active complexes. As can be seen, for procaine and lidocaine the trend is linear between 1×10^{-1} and 1×10^{-3}–10^{-4} M, whereas for papaverine, due to its lower water solubility, the linear region is found between 1×10^{-2} to 1×10^{-4} M. On the other hand, the very bulky complex TPB$^-$–Pap$^+$ presents greater steric hindrance and consequently has more difficulty in reaching the interface. As stated, papaverine hydrochloride has the lowest water solubility of the three cations studied here, while procaine and lidocaine hydrochlorides are very water-soluble. Apparently, this phenomenon is related to their molecular weight; papaverine hydrochloride is 39% heavier than lidocaine and procaine hydrochlorides, the latter having very similar molecular weights. Therefore, papaverine hydrochloride cations that eventually reach the interface have a relatively small tendency to go into the water phase as compared with lidocaine and procaine hydrochlorides.

Fig. 1 also shows a similar behavior for membranes containing just 3 μmol of 1-decanol per membrane. The slopes of the linear part of these plots are summarized in Table 1. As can be observed, their values increase when the membrane contains this aliphatic alcohol. The effect of 1-decanol on the potentiometric electrode behavior is evident and probably is due to a change in the membrane surface polarity caused by the closely packed 1-decanol molecules, which alters the transport of the complexes through a surface barrier formed by alcohol molecules. It is necessary to point out that the molar ratio

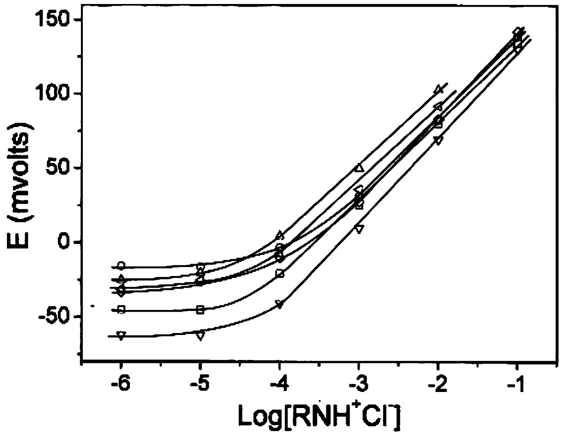

Fig. 1. Calibration curves for RN$^+$H. Without 1-decanol: (∀) procaine, (○) lidocaine, and (8) papaverine. With 3 μmol 1-decanol: (X) procaine, (M) lidocaine, and (Ξ) papaverine.

Table 1
Effect of 1-decanol on $d(E)/d\log([RN^+H])$

Electrode	Without 1-decanol	With 1-decanol
TPB$^-$–Proc$^+$	54.8 ± 0.2	60.2 ± 0.4
TPB$^-$–Lido$^+$	53.8 ± 0.7	57.5 ± 0.5
TPB$^-$–Pap$^+$	53.0 ± 0.9	56.0 ± 0.7