Calix[4]resorcinarene Ionophore in the Ion-Selective Electrodes with Plasticized Poly(vinylchloride) Membranes

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Abstract. Synthetic ionophore calix[4]resorcinarene was incorporated into the poly(vinyl chloride) (PVC) plasticized membrane of an ion-selective electrode (ISE). Calixarene interactions with quaternary ammonium and alkaline metals cations in the organic and water-organic media were carefully investigated by various authors. We studied the effects of choline and Na^+ cations present in the working solution on the ionophore which was incorporated into a membrane phase. Due to the pH sensitivity of the ionophore, a study was undertaken in a wide range of pH values. The different characteristics of calix[4]resorcinarene interactions with these cations were discovered by the ISE with the PVC plasticized membrane containing this ionophore, which respond to both the choline and Na^+ cations due to the variation of working solution pH.

Key words: calix[4]resorcinarene, ion-selective electrode (ISE), choline, sodium ions.

1. Introduction

One of the aims of host-guest chemistry is to construct selective molecular receptors and tools on the 'host-guest pairs' principle. Cyclic host compounds, such as crown ethers, cyclodextrins and calixarenes, were actively modified to obtain new specific binding sites. Calixarenes and calixresorcinarenes were studied as hosts for an extensive spectrum of guests. On the basis of physico-chemical investigations, a number of analytical tools were designed and tested, e.g., for metal cations [1–10], organic compounds – amines and quaternary ammonium ions [10, 11-13] and sugars [14].

Here, we report on the investigation into the interactions between water insoluble calix[4]resorcinarene immobilized in a PVC membrane, and Na^+ and choline cations (Ch^+) present in water solution.

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2. Experimental

2.1. MATERIALS

For plasticized PVC membranes preparation, anhydrous tetrahydrofuran (THF) was used and poly(vinyl chloride) (PVC) powder, *p*-nitrophenyloctyl ether (*p*-NPOE) and sodium tetraphenyl borate (NaTPB), were used without purification. These reagents were a chemical-reagent grade. 2,8,14,20-tetranonyl-4,6,10,12,16,18,22,24- oktahydroxycalix[4]resorcinarene (**I**) was synthesized as described by Tunstad et al. [15].
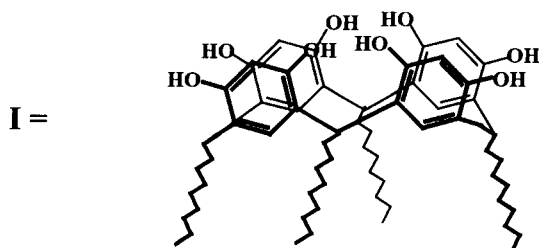
2.2. ISE FABRICATION

An ISE membrane fabrication was used according to Kimura et al. [3]. A composition of 24.3% PVC (120 mg), 65.5% plasticizer, 9.7% calix[4]resorcinarene and 0.5% lipophilic salt NaTPB was dissolved in THF (3 mL) and used to prepare the membrane 50 mm i.d. An Ag/AgCl electrode was used as an internal reference electrode in both the Na^+ and choline selective ISEs. The Na^+-selective ISE contained 10^{-2} M of NaCl as an internal solution, which was subsequently conditioned overnight in a solution of 0.01 M NaCl. The Ch^+-selective ISE contained 10^{-2} M of choline chloride as an internal solution, which was also subsequently conditioned overnight in a solution of 0.01 M choline chloride. All measurements were taken in a 0.01 M TRIS-HCl buffer solution. The measurements were performed at 20 °C using pH/mV ionomer I-130 (Gomel, Bylarussia). As an external reference, a Ag/AgCl, KCl (saturated solution) electrode was used.

3. Results

Two ISEs with identical PVC membranes, Ag/AgCl internal reference electrodes and liquid contacts, were prepared. One of these was filled with 2 mL of internal reference solution of 0.01 M NaCl, and another with 2 mL of 0.01 M choline chloride. The first electrode displayed selectivity towards Na^+ cations, and the second electrode towards both the choline and Na^+ cations.
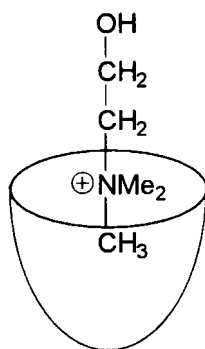
3.1. NA$^+$-SELECTIVE ISE

The response of the ISE with NaCl internal solution on the Na$^+$ cations was observed in a wide range of pH (3.0–9.0), and exhibited a high ISE sensitivity (near the Nernstian slope 57.75 mV/dec) at pH 4.0 and an absence of sensitivity in the basic media (Figure 1a). In the range of pH 5.0–7.0, the sensitivity of the ISE toward Na$^+$ cations, e.g., the slope of the curve, was less than 59 mV/dec. Jump-type characteristics of the response function in the narrow interval of Na$^+$ concentration $(5–8) \times 10^{-3}$ M, and a super-Nernstian slope (79 mV/dec) at pH 3.0, was observed. In basic media, the response of the Na$^+$-selective electrode was too small to be discussed. The response time was about 20 s and remained unchanged irrespective of the working conditions.

3.2. CHOLINE-SELECTIVE ISE

The response of the ISE with internal choline chloride solution on the choline cations was studied at a range of pH 3.0–9.0 (Figure 1b). The pH-dependence was taken at conditions identical for the Na$^+$-selective ISE. The ISE response function had a slope of <59 mV/dec in all cases. In contrast to the Na$^+$-selective ISE, a high sensitivity of the Ch$^+$-selective ISE was observed in the basic medium (pH 9.0). At pH 3.0, the response on Ch$^+$ was not observed and at pH 4.0, the calibration curve had S-like characteristics similar to pH 3.0 for Na$^+$ ISE (slope 30 mV/dec).

According to the data of physico-chemical investigations [16–18] of calixarene complexation, the host-guest-type complexation between Ch$^+$ and **I** was suggested (1).

$$(1)$$

Besides selectivity toward choline, this ISE exhibited selectivity to the Na$^+$ cations. To examine the selectivity of the choline cations towards Na$^+$ ions, a fixed interference method was used. The Ch$^+$-selective ISE response in the pH range of 3.0–9.0, in the presence of 5×10^{-4} M and 1×10^{-3} M NaCl, was studied (Figure 2). The data obtained proved the possibility of determining the Ch$^+$ cations in the presence of the Na$^+$ cations with the choline selective ISE due to the pH variation. The ISE
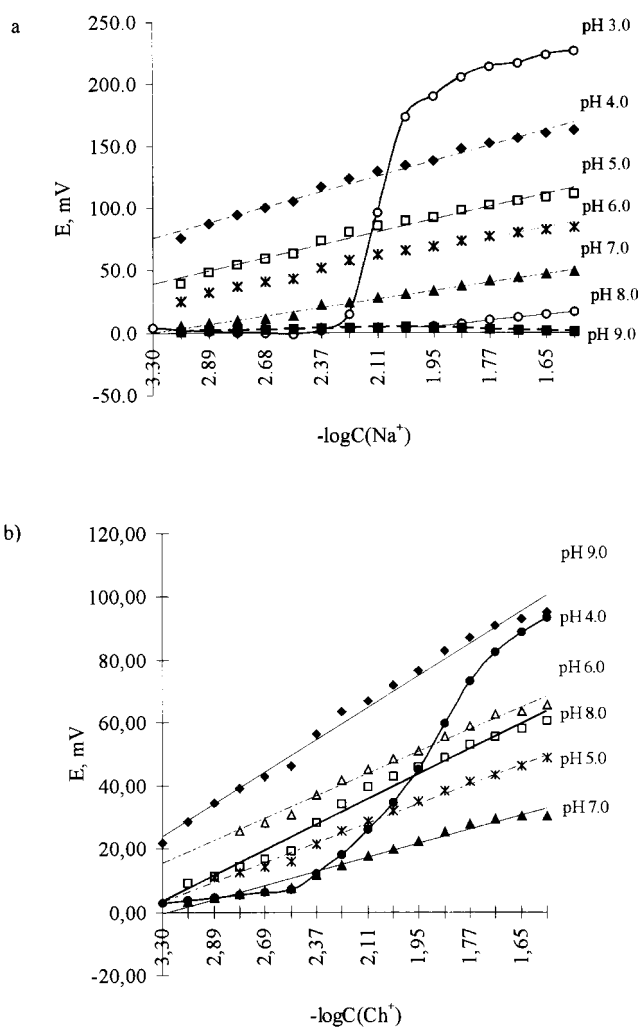
a

b)

Figure 1. The pH-dependence of (a) Na^+-selective ISE response and (b) Ch^+-selective ISE response. 0.01 M TRIS-HCl buffer solution.

sensitivity to the Na^+ cations did not allow us to determine the Ch^+ in acidic media (pH 4.0–6.0), while in basic media (pH 9.0), the Na^+ cations effect on ISE response was not displayed.

4. Discussion

For the development of ISEs, tetra- and hexaethers of calix[4]- or calix[6]arenes are most often used [1–13]. These ISEs exhibited a Nernstian slope and allowed the determination of corresponding guests in the wide range of pH without electrode-function disturbance. Diamond and coworkers used triester monoacid derivatives
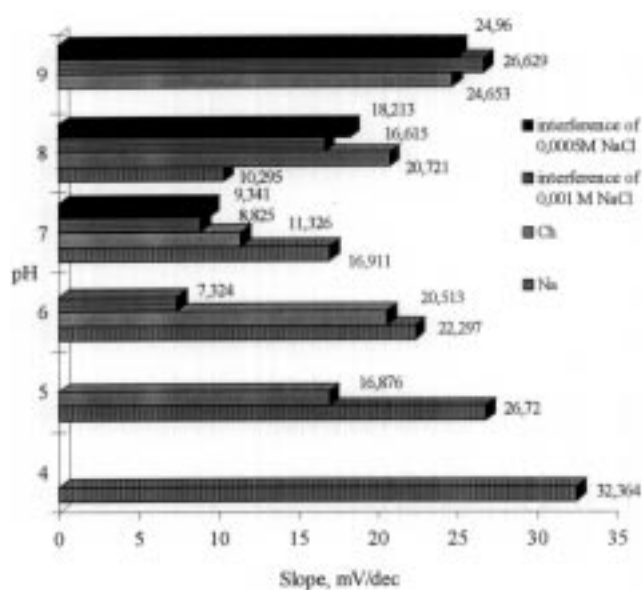
Figure 2. The pH-dependence of the Na$^+$-selective ISE and Ch$^+$-selective ISE slopes.

of *p-tert*-butylcalix[4]arene in the ISE with plasticized PVC membranes [6]. This ionophore, displayed a decrease of the electrode slope in the pH range of 6.0–8.0, due to the presence of the carboxylic group.

According to our data, the value of the electrode slope of <59 mV/dec was ascribed to the H$^+$-ion interactions with the OH groups of the calix[4]resorcinarene, which was called by Schneider et al. [18] a 'proton pump'. Such interactions were reflected in the specific characteristics of the pH-dependence of the ISEs responses. It was reasonable to assume that, in parallel to the Na$^+$ cations, the H$^+$ ions play a role of potential-determining ions because of their influence on the calix[4]resorcinarene ionophore incorporated into the ISE membrane.

In the weak acidic medium, H$^+$ ions of the working solution play the role of potential-determining ions in the plasticized PVC membrane together with the Na$^+$ ions, whereas in the basic medium, the concentration of H$^+$ ions in the bulk solution is much less than that in the membrane body. The size of the Na$^+$ cation allows it to compete with the H$^+$ ions for the calixarene unit, while the larger choline cannot. In the basic media, the absence of the **I**-H$^+$ interactions led to the change of membrane conduction. Probably because that, the decrease of the solution-membrane cations exchange and the ISE response to Na$^+$ cation in the basic media was observed. Contrary to this, the exchange component for the choline cations is not so great because of their rather large size. Thus, the absence of competition with the H$^+$ ions in the basic media increases the number of loaded choline ions and ISE response.

The choline determination-sensitivity decrease at pH 7.0 (Figure 2) was possibly due to the change in the ion conduction of the solution with equivalent H^+ and OH^- ions concentrations: the charge gradient on the phases boundary surface falls and in this case the choline ions played a potential-determining ions role without the H^+ or OH^- ions involvement.

The jump-type response function characteristics, and the super-Nernstian slope at pH 3.0 for Na^+ and S-like characteristics at pH 4.0 for choline cations, was surprising. The 'proton pump' behavior in the basic media accompanying calix[4]resorcinarene OH group ionization was completely studied by Schneider et al. [17, 18]. But how does its OH groups system respond to the excess of free H^+ ions in acidic media? In this case, we assumed that the first horizontal area corresponds to the saturation of the PVC membrane surface by H^+ ions until the choline (or Na^+) cations concentration became sufficient for the competition process to take place. The second horizontal area was ascribed to the membrane surface-saturation by choline (or Na^+) cations, their concentration is in the order of 10 times more than that of the H^+ ions. The observed slope area reflects the transition state between the two described features. Taking the slope values into account in both, the choline and Na^+ cases, the appearance of calix[4]resorcinarene perturbations leading to its simultaneous interaction with Na^+ and H^+ ions, was proposed. In the case of choline, such a process led to the multipoint interaction of one H^+ with the calixarene unit.

5. Conclusions

The effects of the choline and Na^+ cations present in the working solution on the ionophore which was involved in the membrane were studied. The experimental data provided different characteristics of calix[4]resorcinarene interactions with the Na^+ and choline cations. They suggest that we have a complicated competitive system in the ISE membrane, which was sensitive to the presence of Na^+ and choline, as well as to the H^+ ions. The different characteristics of calix[4]resorcinarene interactions with these cations allows us to determine both the choline and Na^+ cations due to the working solution pH variation.

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