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Applicability of a Carrier Based Liquid Membrane pH Electrode to Measurements in Acidic Solutions*

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Abstract

A solvent polymeric membrane electrode based on a synthetic H^+ -carrier is described. The incorporation of the potassium salt of tetrakis(p-chlorophenyl) borate into the membrane phase leads to electrode systems which are suitable for pH measurements in the range 0–4 even in the presence of hydrofluoric acid.

Introduction

The pH electrodes based on H^+ -carriers in polymeric membranes described so far [1, 2] give access to a limited pH-range, i. e. they cannot be used in sample solutions with pH-values below approximately 4 [1, 2]. This most probably is due to anion interference, which can be reduced or may even be eliminated by the incorporation of anionic sites into the membrane phase [3, 4]. Here we report on the behaviour of a solvent polymeric membrane, containing a H^+ -carrier [2] and lipophilic anionic sites in the form of tetrakis (p-chlorophenyl) borate ($TpClPB^-$). Such electrodes can be used to measure pH-values below 4. In contrast to glass electrodes they are tolerant to solutions containing hydrofluoric acid and can easily be miniaturized, e. g. in view of flexible catheter electrodes.

Experimental

Electrode and membrane system

Cells of the type

Ag; AgCl, KCl (satd.)/sample solution//membrane//buffer solution pH 7.0 (40 mM KH_2PO_4 , 23 mM NaOH, 15 mM NaCl), AgCl; Ag

have been used. For measurements in solutions containing hydrofluoric acid a double junction calomel reference electrode (KCl satd.) was used with a 3M KCl solution as bridge electrolyte; this bridge electrolyte was enclosed by a silicone rubber tube, and contact with the sample solution was made via a zirconium oxide diaphragm. The composition of the liquid membranes is: 11.6 wt.-% H^+ -carrier (3-hydroxy-N-dodecylpicolinamide, for synthesis see [5]), 54.0 wt.-% sebacic acid bis (2-ethylhexyl)ester (DOS, Fluka AG, CH-9470 Buchs, techn.) and 34.4 wt.-% poly vinylchloride (PVC S 704, hochmolekular, Lonza AG, CH-3930 Visp) respectively 11.4 wt.-% H^+ -carrier,

1.6 wt.-% potassium tetrakis (p-chlorophenyl) borate ($KTpClPB$, synthesized according to [6]), 53.9 wt.-% DOS and 33.1 wt.-% PVC. The membrane preparation was described earlier [7].

EMF-measurements

The same electronic equipment and experimental setup as described earlier [2] was used. The sample solutions were not buffered and the pH was lowered by stepwise addition of acid. In the case of hydrofluoric acid the fluoride activity of the sample solution was monitored with a fluoride selective electrode (LaF₃ single crystal, Philips-type IS 550). The hydrogen ion activity was assumed to be equal to the fluoride ion activity.

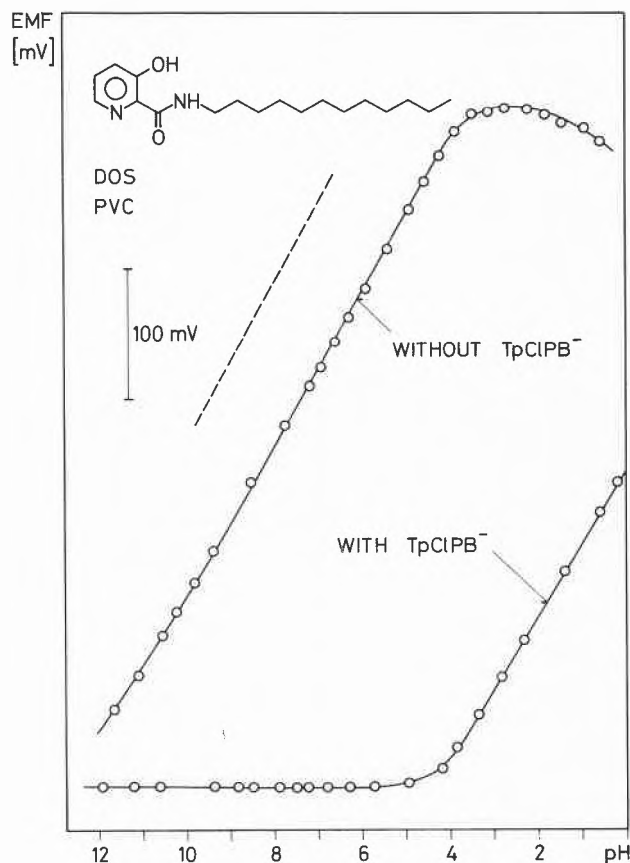


Fig. 1: Influence of lipophilic anionic sites ($TpClPB^-$) in H^+ -carrier based liquid membranes on the pH-response of the electrode. A NaOH solution was acidified stepwise by addition of hydrochloric acid.

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Results and Discussion

The electrode functions presented in Fig. 1 indicate that the incorporation of lipophilic anionic sites (TpClPB⁻) into the membrane phase drastically shifts the range of linear pH response. The loss of response to H⁺-activities at pH-values of the sample solution above 5 is due to cation interference. This is corroborated by the results presented in Fig. 2. An assess-

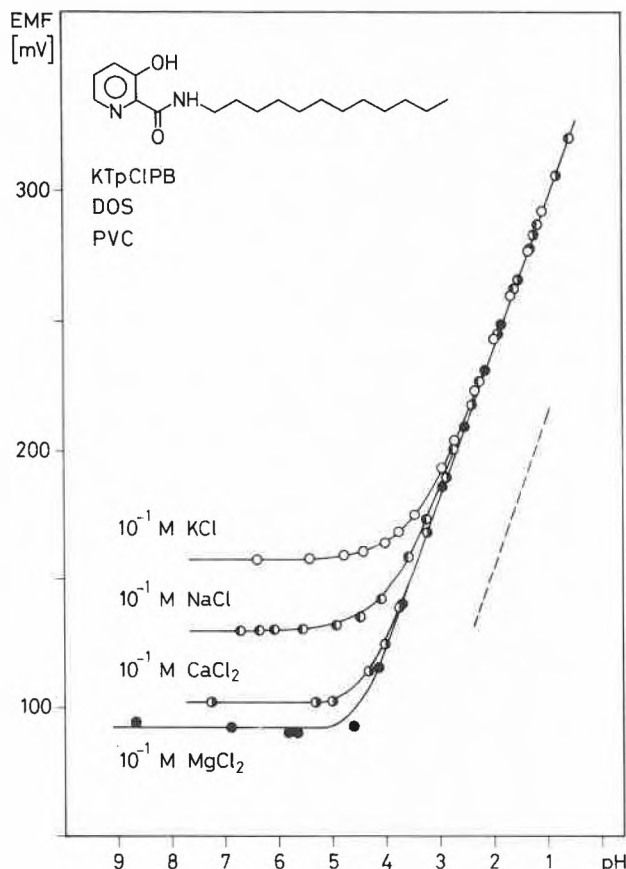


Fig. 2: Response of the cell assembly with a membrane of the given composition to the H⁺-activities at constant concentrations of interfering ions. The pH of the solutions was adjusted using hydrochloric acid.

ment of the selectivity factors $\log K_{HM}^{Pot}$ by the fixed interference method [8] leads to values of -3.0 (M: Na⁺), -2.4 (K⁺), -4.1 (Mg²⁺), and -3.8 (Ca²⁺). The loss in selectivity (see also [2]) is mainly due to the behaviour of TpClPB⁻ as cation exchanger [9]. This is in agreement with the sequence of increasing interference observed: Mg²⁺ < Ca²⁺ < Na⁺ < K⁺. As expected [3, 4], the anion interference becomes more pronounced with increasing lipophilicity of the anions in the sample solution (see Fig. 3). The usefulness of the electrode is limited by high concentrations of very lipophilic anions. It is however especially attractive for use in solutions containing hydrofluoric acid. After continuous contact with a 1 mmol · l⁻¹ HF solution for 13 hours the pH-response of the cell assembly to HCl solutions (Fig. 3) is not affected. In a further possible application of the electrode in

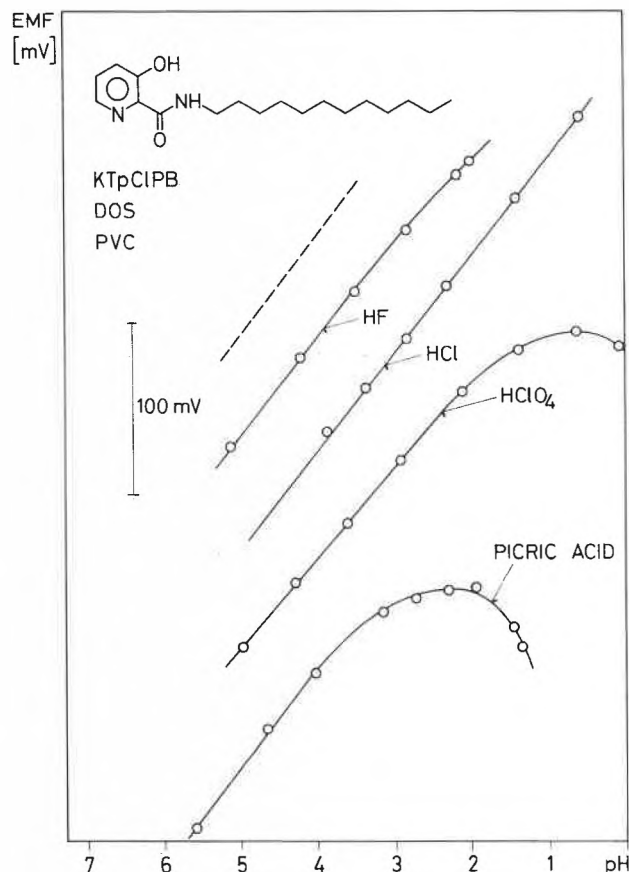


Fig. 3: pH-response of the cell assembly with a membrane of the given composition to solutions containing anions of different lipophilicity.

gastric juice (Na⁺: 58 mmol · l⁻¹, K⁺: 8.4 mmol · l⁻¹, Mg²⁺: 0.47 mmol · l⁻¹, Ca²⁺: 1.0 mmol · l⁻¹ [10]) the interference by the cations mentioned amounts to 0.003 pH units at a pH of 1.98 (see [10]), if the Nicolsky formalism [4] and the presented selectivities are used.

Acknowledgement

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