ESTIMATION METHOD OF H$^+$-SELECTIVE MEMBRANE ELECTRODE DETECTION LIMIT IN HIGHLY ACIDIC SOLUTIONS

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H$^+$-selective electrodes (H$^+$-SE) with ionophore-based plasticized polymeric membranes possess a number of advantages over conventional glass electrodes such as low resistance, which allows for miniaturization, and applicability in hydrofluoric acid solutions. Here we present the results of a study to develop a pH electrode that functions in solutions with pH lower than 1.

According to the theories that describe H$^+$-selective membrane electrodes behavior [1], the extraction of an acid into the membrane phase in acidic solutions assisted by an unprotonated amine form changes the H$^+$ ions activity in the membrane, substantially deviating the electrode response from Nernstian one. At the same time, the E-pH function may go through a maximum.

We have examined the behavior of four H$^+$-SEs with poly(vinylchloride) membranes based on two commercially available ionophores: H$^+$-I (tri-n-dodecylamine) and H$^+$-II (4-nonadecylpyridine), and also on two specially synthesized ionophores: 3,4,5-*tris*(dodecyloxy)benzylbenzylethylamine (S-I) and 3,4,5-*tris*(dodecyloxy)benzylphenylethylamine (S-II) in acidic solutions. Potassium *tetrakis*(4-chlorophenyl) borate and 2-nitrophenyl octyl ether were used as ion-exchanger and plasticizer, respectively. Actually, it is worth determining the limits of detection in solutions of most widespread ions, first of all, in chloride-containing ones. However, chloride-anion is quite hydrophilic, thus, pH-detection limit is achieved only in highly acidic solutions, when an electrode based on S II is used. In these solutions, the diffusion potential is big enough, greatly altering the electrode function. In order to determine the unbiased pH-detection limit we have suggested a new method that involves potential measuring in mixed electrolytes containing an acid and its salt in constant ratio, but different dilutions. The ratio used makes total mobilities of cations and anions equal, thus eliminating the diffusion potential. The difference between maxima for HCl − NaCl and HClO$_4$ − NaClO$_4$ mixtures is ca. 3 logarithmic units and retains constant for different ionophores. This fact provides a feasible way to estimate the pH-detection limit for S-II in chloride-containing solutions that cannot be determined experimentally due to poor solubility of NaCl. The experimental $\lg(a_{\text{H}^+} \cdot a_{\text{ClO}_4^-})_{\max}$ value is 1.1, hence, the corresponding value for chloride is −1.9, that is the pH of 4.5 M HCl solution, taking into account the activity coefficients.

1. V. V. Egorov, Ya. F. Lushchik // Talanta. 1990. V.37. № 5. P. 461.