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SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

# Ion-Selective Membrane Electrode for Determination of the Octahydrotriborate Anion

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**Abstract**—An ion-selective electrode (ISE) based on a plasticized polyvinyl chloride membrane chemically doped with tetradecylammonium octahydrotriborate ($[(C_{10}H_{21})_4N^+][B_3H_8^-]$) has been developed. It is shown that the electrode has a reversible potentiometric response with respect to the octahydrotriborate anion in the presence of a number of other inorganic anions. The influence of the concentration of the electrode-active material and the nature of the plasticizer in the membrane phase on the electrochemical characteristics of the fabricated sensor have been studied. The optimal composition of the ion-sensitive membrane has been found. It has been found that the developed sensor provides a wide range of detectable concentrations of $B_3H_8^-$ ($1 \times 10^{-7}...1 \times 10^{-2}$) and a low detection limit ($10^{-7.3}$ M). The new ISE can be recommended for direct potentiometric detection of free octahydrotriborate anions in technological aqueous solutions.

**Keywords:** octahydrotriborate anion, polymer membrane, tetradecylammonium octahydrotriborate

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## INTRODUCTIONS

Borohydrides have been intensively studied for many years [1–5]. In the family of borohydride compounds, the octahydrotriborate anion $\left(B_3H_8^-\right)$ occupies an intermediate position and is of particular scientific and practical interest, since it is widely used to obtain higher polyhedral borohydrides and is also a key intermediate in the dehydrogenation of many borohydrides [6–11]. However, despite the fact that $B_3H_8^-$ has been well studied, its quantitative determination in aqueous solutions has been studied scarcely [12, 13]. An effective approach to solving this problem seems to be the use of a membrane ion-selective electrode (ISE), which is reversible with respect to $B_3H_8^-$ solutions [14–17]. It should be noted that, at present, ISEs based on polymer membranes, being an important variety of potentiometric sensors, are successfully used for express control of the content of various ions in natural and technological solutions [14–17]. This is primarily due to their remarkable availability in terms of ease of instrumentation and low cost of analysis, as well as the fact that they have practically no effect on the analyzed solution.

The purpose of this work is to create an ISE based on tetradecylammonium octahydrotriborate ($[(C_{10}H_{21})_4N^+][B_3H_8^-]$) introduced into a plasticized polyvinyl chloride membrane (PVC membrane) and to study the possibility of using it for potentiometric determination of the activity (concentration) of free ions in aqueous solutions. The analytical signal of the ISE recorded under conditions close to zero current and corresponding to the measurement of the magnitude of the electromotive force (e.m.f. $= \Delta E = E_{\text{ISE}} - E_{\text{ES}}$) of the electrochemical system will provide express detection of $B_3H_8^-$ in a wide concentration range and relative ease of interpretation of the results obtained.

## EXPERIMENTAL

**Reagents and solutions.** The starting reagents were of pure for analysis and chemically pure grades (Russian State Standards): 2-nitrophenyloctyl ether (*o*-NPOE), dibutyl phthalate (DBP), tris(2-ethylhexyl) phosphate (TEHP), bis(1-butylpentyl)adipate (BBPA), as well as tetradecylammonium bromide, polyvinyl chloride (PVC, high molecular weight, Selectophore, Fluka), methylene chloride ($CH_2Cl_2$), and freshly distilled tetrahydrofuran (THF). Cesium octahydrotriborate $Cs[B_3H_8]$ was synthesized and identified in the Laboratory of Chemistry of Light Elements and Clusters, the Kurnakov Institute RAS

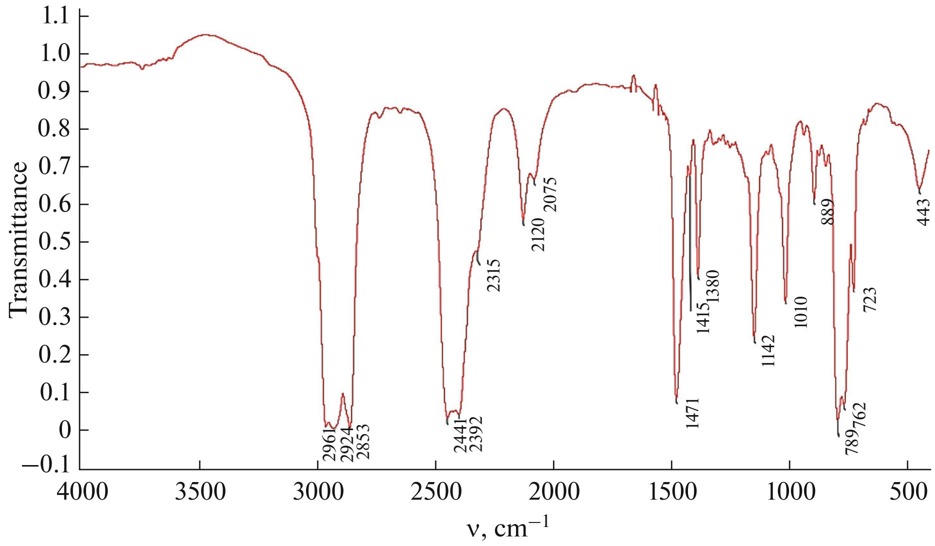

**Fig. 1.** IR spectrum of the prepared sample of tetradecylammonium octahydrotriborate.

[18, 19]. The stock solution of Cs[$B_3H_8$] (0.1 M) was prepared by dissolving an accurate weighed portion of the preparation Cs[$B_3H_8$] (1.734 g) in 100 mL of deionized water. The remaining working solutions ((0.01–1) × $10^{-8}$ M) were prepared by successive dilutions of the stock solution.

**Preparation of the electrode-active material (EAM).** Tetradecylammonium octahydrotriborate was obtained by liquid ion-exchange extraction:

$$[(C_{10}H_{21})_4N]^+[Br]^- + Cs^+[B_3H_8]^- \rightleftarrows CsBr + [(C_{10}H_{21})_4N]^+[B_3H_8]^-.$$

For this purpose, 20 mL of a 0.01 M solution of tetradecylammonium bromide in $CH_2Cl_2$ was mixed with 25 mL of a 0.01 M aqueous solution of cesium octahydrotriborate. The organic phase was separated in a separating funnel and washed with 100 mL of water. The degree of substitution of bromide ions in the initial salt was determined by controlling their content in the aqueous phase using a bromide ISE with a solid membrane based on a mixture of silver sulfide and bromide. After a double extraction, the quantitative substitution of bromide ions by anions $B_3H_8^-$ in the organic phase was recorded. The resulting organic phase was transferred to a Petri dish. After removal of methylene chloride at room temperature, tetradecylammonium octahydrotriborate [$(C_{10}H_{21})_4N$][$B_3H_8$] was obtained as a white powder, which was used as EAM. The chemical composition of the powder was confirmed by elemental chemical analysis, IR and $^{11}B$ NMR spectroscopies (Figs. 1, 2).

The absorption bands at 1390 and 1470 cm$^{-1}$ were attributed to bending vibrations of C–H methyl and methylene groups, and the intense absorption band at 720 cm$^{-1}$ was assigned to vibrations of carbon chains of the $[-CH_2-]_n$ type at $n > 4$ (Fig. 1). The absorption band at 910 cm$^{-1}$ is characteristic of the $B_3H_8^-$ anion [19]. The multiplet recorded in the $^{11}B$ NMR spectra with the chemical shift $\delta = -29.0$ indicates the presence of boron in the octahydrotriborate anion (Fig. 2a).

**Production of ISE with plasticized PVC membranes.** To obtain plasticized PVC membranes, a previously developed technique was used [20]. An accurate weight of EAM was first dissolved in a plasticizer and then mixed with a pre-prepared solution of PVC in THF. The resulting mixture was thoroughly mixed and transferred into a glass ring with an inner diameter of 28 mm, located on a smooth glass surface. The top of the ring was covered with a 5 mm layer of filter paper, which was pressed down with a lead weight (for uniform evaporation of THF from the surface). After evaporation of THF in a thermostat at 32°C for 48 h, the membrane was kept under vacuum for 60 min. As a result, a transparent polymer film with an average thickness of ~0.3 mm was obtained. Then, disks 9.5 mm in diameter were cut out of it and placed in a standard Philips IS 561 electrode housing. Before work, the fabricated sensor was kept in a 1 × $10^{-4}$ M Cs[$B_3H_8$] solution for 15–30 min.

**Methods of analysis and equipment.** Potentiometric measurements were carried out using a Radelkis OP-300 pH-ion analyzer using a galvanic circuit of the following type:

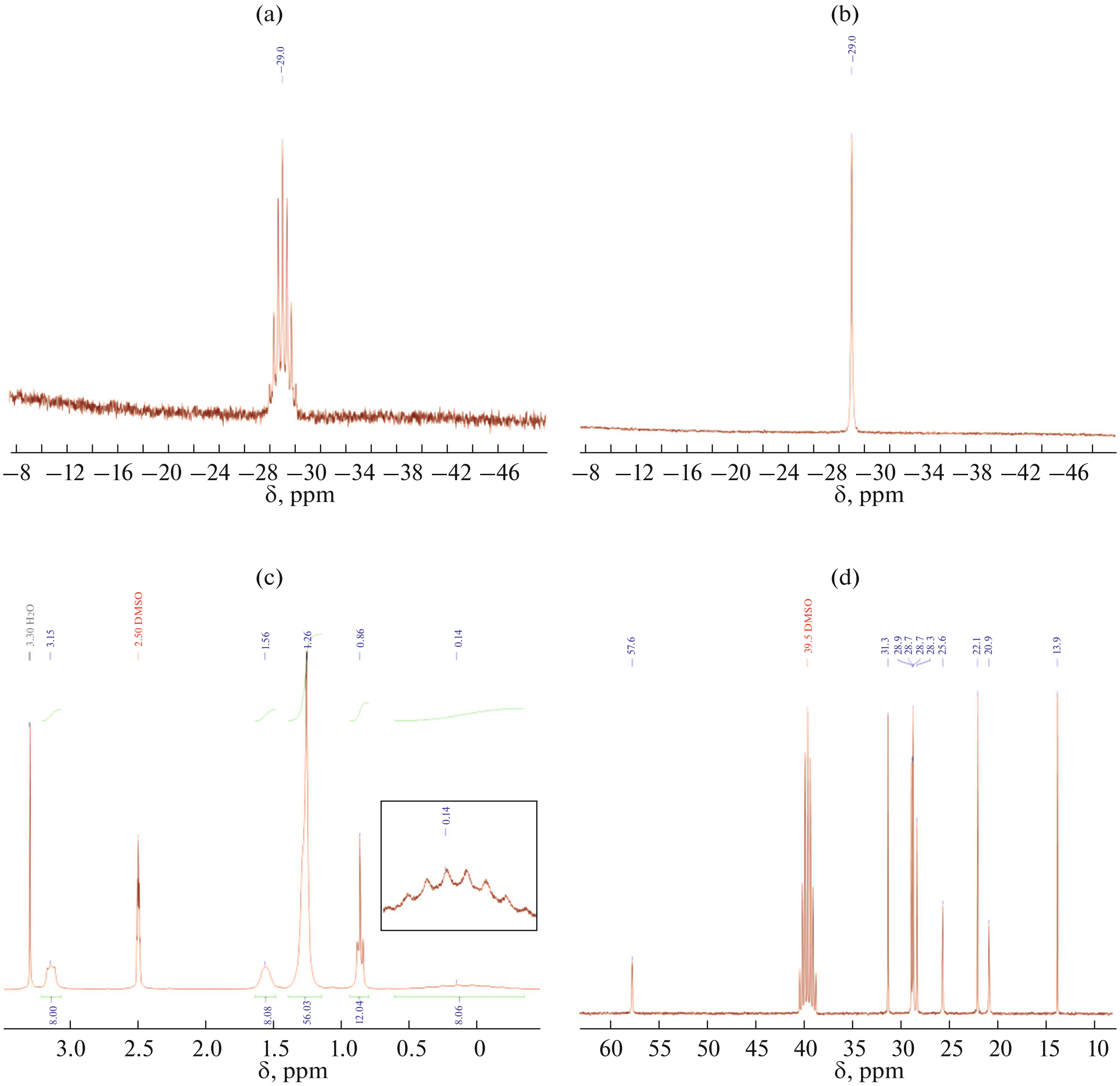

**Fig. 2.** NMR spectra characterizing the sample of tetradecylammonium octahydrotriborate: (a) $^{11}B$ NMR, (b) $^{11}B$-{$^{1}H$} NMR, (c) $^{1}H$ NMR, (d) $^{13}C$ NMR.

Ag/AgCl | 3 M KCl, $AgCl_{saturated}$ | Tested solution | Membrane | Internal reference solution | AgCl/Ag

A $1 \times 10^{-3}$ M potassium perchlorate solution was used as the internal reference solution, which was chosen taking into account the rather low hydration energy of the perchlorate anion. The external reference electrode was a Radelkis OP-0820 silver chloride electrode. The electrode function was recorded in the range $1 \times 10^{-8}...1 \times 10^{-1}$ M using freshly prepared solutions of $Cs[B_3H_8]$, starting from solutions with a lower anion concentration. The electrode potential was recorded as the arithmetic mean of three values differing by no more than 0.5 mV. The test solutions were mixed with a magnetic stirrer. The temperature during measurements was 25 ± 1°C.

Elemental analysis of EAM for the content of carbon and hydrogen was performed on a CHNS_3 FA 1108 Elemental Analyzer automatic gas analyzer

**Table 1.** Dependence of the potentiometric characteristics of ISE obtained in Cs[$B_3H_8$] solutions on the concentration content of EAM in the membrane phase

| Membrane composition, wt % | | | $c_{\min}$, M | $s$, mV/decade | Linear concentration response range, M | Drift capacity, mW/h |
|---|---|---|---|---|---|---|
| EAM | PVC | DBP | | | | |
| 0.5 | 29.0 | 70.5 | $\approx 9 \times 10^{-8}$ | 59.0 | $1 \times 10^{-7}$–$1 \times 10^{-2}$ | ±(2–4) |
| 0.8 | 29.0 | 70.2 | $5 \times 10^{-8}$ | 57.9 | $8 \times 10^{-8}$–$1 \times 10^{-2}$ | ±0.2 |
| 1.0 | 29.0 | 70.0 | $3 \times 10^{-7}$ | 55.4 | $5 \times 10^{-7}$–$1 \times 10^{-2}$ | ±0.1 |

(Carlo Erba). IR spectra were obtained on an INFRALUM FT-02 IR Fourier spectrometer in the range 400–4000 cm$^{-1}$. Samples were prepared by dispersing the test substance in liquid paraffin or Fluorolube fluorinated oil. $^{1}$H, $^{11}$B, $^{13}$C NMR spectra of [$(C_{10}H_{21})_4N$][$B_3H_8$] solutions in DMSO-$d_6$ were recorded on a Bruker MSL-300 pulsed Fourier spectrometer (Germany) at frequencies of 300.3, 96.32, and 75.49 MHz, respectively, with internal deuterium stabilization. Tetramethylsilane and boron trifluoride etherate were used as external standards.

## RESULTS AND DISCUSSION

Previous studies have shown that a promising way to create membrane ISEs with an anionic function is the use of electrode-active substances with predictable ion-exchange properties. To determine the activity (concentration) of inorganic anions in liquid media, electrodes based on membranes doped with EAMs with charged active centers (ionic associates with large organic cations capable of dissociating to some extent in the membrane phase) are most widely used [21–23]. In particular, ionic associates of higher quaternary ammonium bases with different steric accessibility of the exchange center have proven themselves as EAMs in anion-selective electrodes [24–26]. In this regard, we fabricated an ISE with a PVC membrane containing an associate of the octahydrotriborate anion with tetradecylammonium ([$(C_{10}H_{21})_4N$][$B_3H_8$]) and studied its behavior in aqueous solutions of the Cs[$B_3H_8$] salt.

The classical ISE polymer membrane is a three-component composition: EAC–plasticizer–polymer matrix, the properties of which largely depend on the nature and ratio of the membrane-forming components. At the same time, the electroanalytical parameters of sensors based on ion associates significantly depend on both the EAM content and the nature of the plasticizer in the membrane phase. The selectivity of the potentiometric response of such sensors is usually determined by the hydration (solvation) energy of the anion being determined and the specificity of its interaction with the binding site [27]. Therefore, when developing a new ISE, we focused on optimizing the composition of the ion-sensitive PVC membrane.

### *Choice of EAM Concentration*

As a result of studying the dependence of the potentiometric response of ISEs fabricated on the basis of a PVC membrane plasticized with DBP and containing different amounts of [$(C_{10}H_{21})_4N$][$B_3H_8$], it was found that the sensor containing 0.8 wt % EAM shows the best results with respect to the $B_3H_8^-$ ion (Table 1).

With an increase in the EAM content in the polymer composition, a deterioration in the lower detection limit ($c_{\min}$) of the octahydrotriborate ion in solution was observed, which can be explained by an increase in the activity of the potential-determining anion in the surface membrane layer relative to the aqueous solution. With a decrease in the content of EAM in the polymer composition, an instability of the recorded potential was observed. The latter is probably associated with a decrease in ion-exchange centers in the membrane phase.

### *Dependence of Electrode Response on Nature of the Plasticizer*

Another important parameter to consider in order to achieve the best performance of ion sensitive sensors is the nature of the plasticizer used in the membrane. The plasticizer, which, as a rule, makes up >60% of the mass composition of the membrane, serves as a solvent for membrane-forming compounds, determines the degree of association of the resulting ion pairs, and ensures its dielectric and mechanical properties [28–30]. As plasticizers, we studied DBP, *o*-NPOE, BBPA, and TEHF, which differ in the nature of active groups, radical length, and dielectric permittivity. When comparing, we used the ratio of membrane components corresponding to the following composition of the membrane phase (wt %): EAM, 0.8; plasticizer, 70.2; and PVC, 29.0. The results obtained in the study of the influence of the nature of the plasticizer on the potentiometric response with respect to ions $B_3H_8^-$ are shown in Fig. 3 and summarized in Table 2.

According to the obtained experimental data, all manufactured sensors showed almost the same range of electrode function linearity. However, the slope coefficient (slope $S$) and the range of performance of

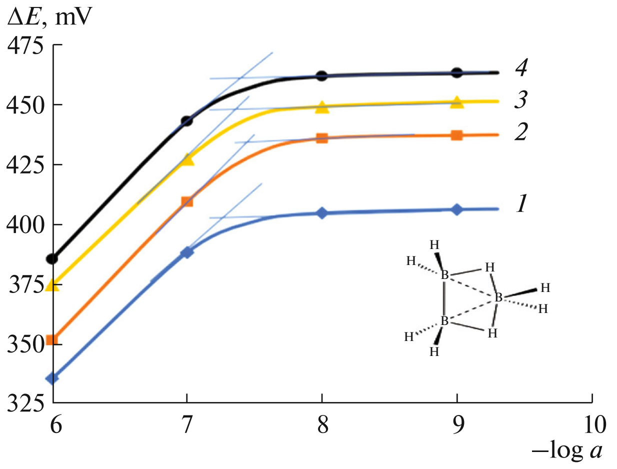

**Fig. 3.** Electrode functions of ISEs based on PVC membranes containing $[(C_{10}H_{21})_4N]^+[B_3H_8]^-$ and various plasticizers in dilute $Cs[B_3H_8]$ solutions. Plasticizers: (*1*) *o*-NPOE; (*2*) DBP; (*3*) TEHF; (*4*) BBPA.

the electrode function in the region of diluted $Cs[B_3H_8]$ solutions were found to be dependent on the nature of the plasticizer. The best results in terms of the steepness of the electrode function were demonstrated by sensors containing DBP ($\varepsilon_\gamma = 6.4$) and BBPA ($\varepsilon_\gamma = 5.3$). In contrast, sensors fabricated using more polar plasticizers such as TEHF ($\varepsilon_\gamma = 9.9$) and *o*-NPOE ($\varepsilon_\gamma = 21.0$) showed a sub-Nernstian slope. The lowest value of the lower limit of detection of $B_3H_8^-$ was established for ISE based on DBP, the highest value was found for *o*-NPOE. It is obvious that when the plasticizer is replaced, the degree of association of the $[(C_{10}H_{21})_4N]^+[B_3H_8]^-$ ion pair in the membrane phase and the activity (free concentration) of ions $B_3H_8^-$ at the membrane/solution interface change.

Figure 4 shows a diagram characterizing the potentiometric selectivity coefficients calculated for the studied membrane systems with the best electrode characteristics by the method of mixed solutions [31].

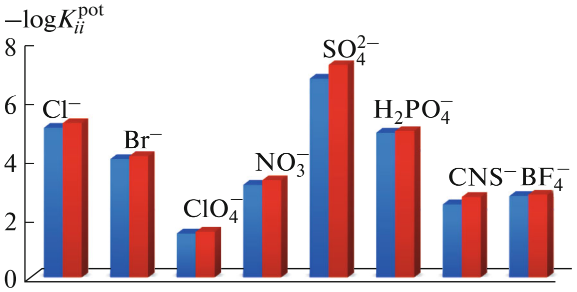

**Fig. 4.** Potentiometric selectivity coefficients of ISEs based on PVC membranes plasticized with DBP (blue) and BBPA (red).

It can be seen that the electrodes under study show selectivity with respect to $B_3H_8^-$. In this case, the order of change $\log K_{i,j}^{\text{pot}}$ corresponds to the known scale of extractability of inorganic anions by quaternary ammonium bases, starting from lipophilic $ClO_4^-$ and ending with hydrophilic $SO_4^{2-}$ [32].

### *Dependence of Potentiometric Response on pH of Studied Aqueous Solution*

To estimate the working pH range of the fabricated sensor with the optimal composition of the membrane plasticized with DBP, the dependence of the electrode potential in $1 \times 10^{-3}$ M $Cs[B_3H_8]$ solutions in the pH range from 2 to 9 was obtained. Figure 5 shows that the potentiometric response of the sensor is practically independent of the pH of the test solution at pH 4.8–7.5. This confirms the known data that aqueous solutions of salts of octahydrotriborate ions have rather high stability [33]. However, at $4.5 \le \text{pH} \ge 7.8$, some increase in the electrode potential is observed, indicating a decrease in the free concentration of $B_3H_8^-$ in alkaline and acidic media.

Based on the data obtained, it can be concluded that the developed ISE with a plasticized PVC mem-

**Table 2.** Characteristics of the potentiometric response of the studied ISEs depending on the nature of the plasticizer in the membrane phase

| Plasticizer | Regression equation | Linearity range, M | $c_{\min}$, M |
|---|---|---|---|
| DBP | $\Delta E = 57.92 \log a + 4.79$<br>$(R^2 = 0.9997)$ | $1 \times 10^{-2}$–$8 \times 10^{-8}$ | $10^{-7.3}$ |
| BBPA | $\Delta E = 58.81 \log a + 33.04$<br>$(R^2 = 0.9999)$ | $1 \times 10^{-2}$–$9 \times 10^{-8}$ | $10^{-7.2}$ |
| *o*-NPOE | $\Delta E = 52.54 \log a + 21.12$<br>$(R^2 = 0.9983)$ | $1 \times 10^{-2}$–$1 \times 1\ 0^{-7}$ | $10^{-7.0}$ |
| TEHP | $\Delta E = 54.19 \log a + 49.43$<br>$(R^2 = 0.9992)$ | $1 \times 10^{-2}$–$1 \times 10^{-7}$ | $10^{-7.1}$ |

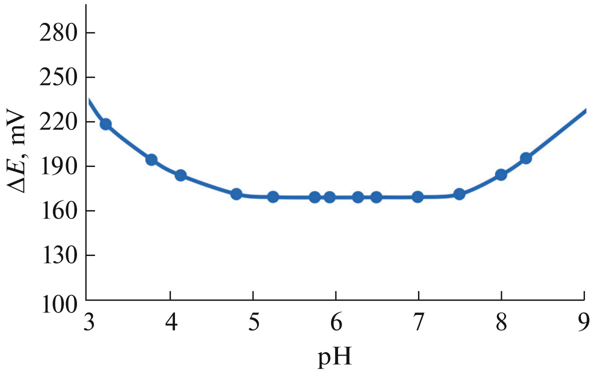

**Fig. 5.** Dependence of the potentiometric response of an ISE with a membrane based on DBP on the pH of an aqueous solution containing $1 \times 10^{-3}$ M $Cs[B_3H_8]$.

brane containing $[(C_{10}H_{21})_4N][B_3H_8]$ as an EAM is characterized by high sensitivity and selectivity with respect to in the presence of a number of inorganic anions in a wide pH range of an aqueous solution. The developed electrode can be recommended for express analysis of technological aqueous solutions.

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## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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