Preparation and Properties of Membrane Caesium Ion-Selective Electrode

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Electrochemical properties of heterogeneous poly(vinyl chloride) membrane containing electrically active caesium cobalt nitrite ($Cs_3Co(NO_2)_6 \cdot 2H_2O$) and dibutyl phthalate as plasticizer were studied. Slope of the ionic function of the ion-selective electrode made of this membrane was 40—43 mV/pCs. Dependence of EMV on the concentration of caesium ions was found to be linear in the 5×10^{-2} to 10^{-4} mol dm^{-3} range. Apparent potentiometric coefficients of selectivity for cations Li^+, Na^+, K^+, Rb^+, NH_4^+, Ag^+, Mg^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, and Fe^{3+} were estimated by the separate solutions method. The pH of solutions within 4.5 and 9.5 did not influence the electrode response.

Ion-selective electrodes are of permanent interest for their simplicity, low demandingness, reasonable prices, and a wide application area. Of interest are also membrane electrodes containing various electroactive compounds. Activity of caesium ions was measured with potassium ion-selective electrodes [1, 2] or membrane silicone rubber ones containing caesium 12-molybdatophosphate [3, 4], liquid membrane electrodes with caesium tetraphenylborate [5, 6], or membrane electrodes with electroactive crown-ethers [7].

This paper concerns investigation of properties of membrane caesium ion-selective electrode made of poly(vinyl chloride) and a little soluble caesium salt $Cs_3Co(NO_2)_6 \cdot 2H_2O$.

EXPERIMENTAL

All reagents (Lachema, Brno) were of anal. grade; poly(vinyl chloride), suspension Slovinyl, batch No. R-452, type 703 (Research Institute for Petrochemistry, Prievidza) was used for preparation of membranes. The electroactive substance was prepared by precipitation of 0.1 M-$Na_3Co(NO_2)_6$ (100 cm^3) with 1 M-$CsNO_3$ (100 cm^3) with stirring. The yellow precipitate was filtered off, washed and dried. Elemental and thermal analyses corroborated the compound to be $Cs_3Co(NO_2)_6 \cdot 2H_2O$. The membrane was prepared by dissolving the powdered poly(vinyl chloride) (200 mg) containing caesium cobalt nitrite (5—50 mg) in cyclohexanone and dibutyl phthalate as plasticizer. The homogenized mixture was poured into a Petri dish and the solvents were allowed to evaporate at room temperature. The heterogeneous membrane thus formed (thickness 0.2—0.3 mm) was cut into disks (diameter 14 mm), which were pasted on a poly(vinyl chloride) support plate and inserted into ammonia gas-electrode carrier, type 10-23 (Monocrystals, Turnov). The inner reference electrode consisted of silver chloride electrode immersed in 0.1 M-$CsNO_3$. This caesium membrane ion-selective electrode was conditioned in 0.1 M-$CsNO_3$ for 24 h prior to measurement and also stored in this solution.

The electromotoric voltage (EMV) between the cell constructed of caesium ion-selective electrode and reference silver chloride electrode with salt bridge, type RAE 112 (Monocrystals, Turnov) was measured with a Precise digital pH-meter, type OP 208/1 (Radelkis, Budapest). The pH was measured with glass electrode, type OP 0808P. Measured were mechanically stirred solutions. Calibration 5×10^{-2}—10^{-6} M-$CsNO_3$ solutions were obtained by diluting the stock 0.1 M solution; pH was adjusted by addition of 0.1 M- and 1.0 M-HNO_3 or -LiOH, respectively.

RESULTS AND DISCUSSION

Influence of the amount of electroactive substance in the poly(vinyl chloride) membrane on the electrode response was investigated; the best results were obtained with membranes composed of $Cs_3Co(NO_2)_6 \cdot 2H_2O$, poly(vinyl chloride), and dibutyl phthalate in 1 : 10 : 10 and 1 : 20 : 20 mass ratios. The slope value for the electrode ionic function with these membranes was 40–43 mV/pCs. Dependence of the given electromotoric cell voltage is linear in the 5×10^{-2}—10^{-4} mol dm^{-3}

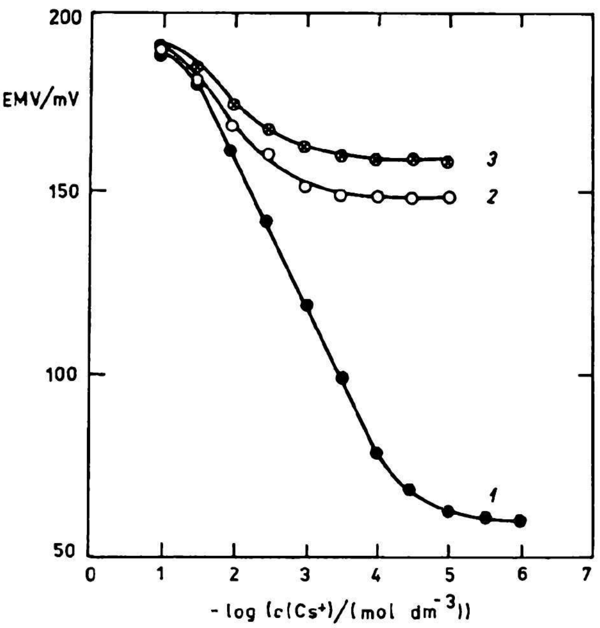

Fig. 1. Dependence of EMV of the cell formed of the membrane caesium ion-selective electrode made of poly(vinyl chloride), plasticizer, and the electroactive substance in a 10 : 10 : 1 mass ratio and reference Ag/AgCl electrode on concentration of Cs^+ ions; T = 298 K, pH = 5—6. *1.* Without interfering ions; *2.* in the presence of 0.01 M-$LiNO_3$; *3.* in the presence of 0.01 M-KNO_3.

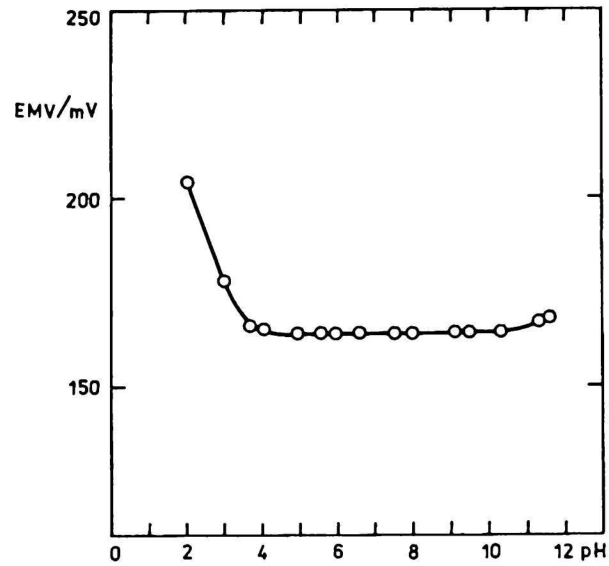

Fig. 2. Dependence of EMV of the membrane caesium ion-selective electrode *vs.* reference Ag/AgCl electrode on the pH of 0.01 M-$CsNO_3$ (T = 298 K).

concentration range of Cs^+ ions (Fig. 1), the correlation coefficient and the standard deviation being 0.998 and 1.2930, respectively.

Ag | AgCl | 0.01 M-KCl | 0.1 M-$CsNO_3$ | caesium membrane electrode | solution measured | 0.1 M-KNO_3 | saturated KCl | Ag | AgCl

The electrode potentials were reproducible up to 3 mV within 10 measurements. The response time of the electrode [8] depended on the concentration of caesium ions; thus, at 10^{-1}—10^{-2}, 10^{-3}—10^{-4} and 10^{-5} mol dm^{-3} it was 30 s, 1 and 2 min, respectively. The pH value of calibration solutions ranged within 5 and 6, that of the electrode inner resistance was 25—30 MΩ.

Influence of pH of the solutions on the response of the caesium ion-selective electrode is seen in Fig. 2. The EMV of the cell is constant in the pH range 4.5—9.5, whilst the voltage rises considerably at pH = 4—2. Above pH 9.5 the EMV increase is mild, which can probably be due to the interference of Li^+ cations from the solution (employed for adjusting the pH).

The effect of interfering ions was examined by the separate solutions method [9, 10]. Apparent potentiometric selectivity coefficients were estimated for ions Li^+, Na^+ K^+, Rb^+ NH_4^+, Ag^+ Mg^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, and Fe^{3+} (Table 1). The value of apparent potentiometric selectivity coefficients was calculated employing the equation

$$\log K_{\mathrm{Cs,M}}^{\mathrm{pot}} = \frac{E_\mathrm{M} - E_\mathrm{Cs}}{S} + \log \frac{a_\mathrm{Cs}}{a_\mathrm{M}^{1/z}} \qquad (1)$$

where E_M and E_Cs are electromotoric voltages of cells formed of the caesium ion-selective and reference electrodes immersed into the appropriate solutions of interfering ions, or caesium nitrate, S stands for the experimentally determined slope of caesium ion-selective electrode and z is the charge characteristics of the interfering ion.

Table 1. Apparent Potentiometric Selectivity Coefficients of Caesium Ion-Selective Electrodes

Interfering ion	$K_{\mathrm{Cs,M}}^{\mathrm{pot}}$	$K_{\mathrm{Cs,M}}^{\mathrm{pot}}$ [3]	$K_{\mathrm{Cs,M}}^{\mathrm{pot}}$ [6]
Li^+	4×10^{-1}	1.2×10^{-1}	2×10^{-4}
Na^+	4.8×10^{-1}	7×10^{-2}	4×10^{-4}
K^+	6.7×10^{-1}	7.4×10^{-1}	3×10^{-2}
Rb^+	7.1×10^{-1}	4.26×10^{2}	–
NH_4^+	7.7×10^{-1}	6.3	6×10^{-3}
Ag^+	1.4	–	2×10^{1}
Mg^{2+}	7.5×10^{-2}	–	3×10^{-5}
Ca^{2+}	8.2×10^{-2}	–	8×10^{-5}
Co^{2+}	7.7×10^{-2}	–	3×10^{-4}
Ni^{2+}	7.1×10^{-2}	–	4×10^{-5}
Fe^{3+}	2.8×10^{-1}	–	–

Interfering solutions of the respective nitrates, used for determination of the apparent potentiometric selectivity coefficients, had to have the same activity as the caesium ions (10^{-2} mol dm^{-3}). Selectivity of the caesium electrode made by us was lower than that described by *Baumann* [6], and also the influence of interfering Rb^+ and NH_4^+ ions was considerably lower when compared with that reported in Ref. [3]. As found, the Ag^+ and Fe^{3+} ions exerted a noticeable interference.

The membrane caesium ion-selective electrode is suitable for determination of caesium ions in aqueous solutions in the concentration range 5×10^{-2}—10^{-4} mol dm^{-3} at pH = 4.5—9.5. Lower concentrations (10^{-5}—10^{-6} mol dm^{-3}) require supplementary calibration. Advantage of the electrode under study is the higher slope value in relation to that described in Ref. [3] (24.5 mV), and a relative construction easiness.

REFERENCES

1. Davies, J. E. W., Moody, G. J., Price, W. M., and Thomas, J. D. R., *Lab. Pract. 22,* 20 (1973).
2. Orion, *Analytical Methods Guide.* 5th Edition. 1972.
3. Coetzee, C. J. and Basson, A. J., *Anal. Chim. Acta 57,* 478 (1971).
4. Coetzee, C. J. and Basson, A. J., *Anal. Chim. Acta 56,* 321 (1971).
5. Ruzicka, J. and Tjell, J. C., *Anal. Chim. Acta 49,* 346 (1970).
6. Baumann, E. W., *Anal. Chem. 48,* 548 (1976).
7. Kimura, K. and Shono, T., *Proceedings of the 4th Symposium on Ion-Selective Electrodes.* Matrafüred, 1984.
8. IUPAC Commission of Analytical Nomenclature, *Pure Appl. Chem. 48,* 127 (1976).
9. Eisenman, G., Rudin, D. O., and Cashby, J. U., *Science 126,* 871 (1957).
10. Rechnitz, G. A. and Kresz, M. R., *Anal. Chem. 38,* 1786 (1966).

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