

Reagents

High molecular weight poly(vinyl chloride) (PVC), 2-nitrophenyl octyl ether (NPOE), (bis-(2-ethylhexyl) sebacate (DOS), 2-fluorophenyl-2-nitrodiphenyl ether (FNDPE), tris-(2-ethylhexyl) phosphate (TOP), bis(2-ethylhexyl) phthalate (DOP), tetrakis-(trifluoromethyl)phenyl borate (KTTFMPB), Calcium ionophore I ((-)-(R,R)-N,N'-bis-[11-(ethoxycarbonyl)undecyl]-N,N'-4,5-tetramethyl-3,6-dioxaoctanediamide)) and Magnesium ionophore I (N,N'-Diheptyl-N,N'-dimethyl-1,4-butanediamide), were purchased from Fluka (Switzerland). Chlorinated cobalt dicarbollide (CCD) was obtained from Katchem (Czech Republic) as a cesium salt and then converted to the acidic (H⁺) form prior to the membrane preparation.

NaCl, CaCl₂, MgCl₂ metal chloride salts were purchased from Vekton (Russia, analytical grade). Tetrahydrofuran (THF) purchased from Merck (Germany) was freshly distilled before use.

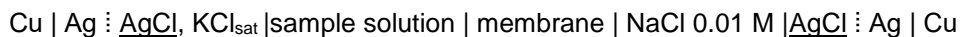
Membrane preparation

The ionophore-free polymeric membranes consisted of 33 wt% PVC, 66 % plasticizer and 1 % of a lipophilic additive. All ten compositions studied in this paper are described in details in the Table 1. To prepare the membrane, the components (300 mg in total) were dissolved in 3 mL of THF, poured into a Teflon cylindrical vessel and left to dry for 48 h. Then membranes of 7 mm in diameter (three of each composition) were cut from the resulting film and glued to a PVC tube body.

Potentiometric measurements

The sensor set comprised 30 cross-sensitive cationic sensors (10 types, 3 pieces of each kind).

Electrochemical measurements were carried out in the following galvanic cell:



The EMF measurements were performed against the standard reference Ag/AgCl (ZIP, Belorussia) electrode at room temperature (20 °C) using a multi-channel digital mV-meter with high input impedance (Sensor Systems, Russia). The potential values were recorded with the 0.1 mV precision for 3 minutes in 10 sec intervals. The results were presented as an average of the last 3 EMF values during these 3 minutes.

The glass pH electrode (ZIP, Belorussia) was used for pH control.

Activity coefficients were calculated according to Debye–Hückel theory.

Calibration of the sensors was performed in chloride salts Ca²⁺- and Mg²⁺ solutions in the concentration range between 10⁻⁷ and 10⁻² M. The sensor sensitivity was calculated as a slope of the electrode response (mV per decade) for the metal ion concentration range between 10⁻⁴ and 10⁻² M. All calculated slopes were averaged over the three replica sensors of each composition and multiple replicated measurements.

To assess the correlation between the array response and the Ca²⁺ and Mg²⁺ concentration, the calibration was performed for the sample set containing 40 binary Ca-Mg mixtures (Set 1).

Table 1. Composition of the membranes

Name	Plasticizer	Lipophilic salt
1	2-nitrophenyl octyl ether (NPOE)	Tetrakis(trifluoromethyl)phenyl borate (KTTFMPB)
2	2-nitrophenyl octyl ether (NPOE)	chlorinated cobalt dicarbollide (CCD)
3	di(2-ethylhexyl) sebacate (DOS)	Tetrakis(trifluoromethyl)phenyl borate (KTTFMPB)
4	di(2-ethylhexyl) sebacate (DOS)	chlorinated cobalt dicarbollide (CCD)
5	2-fluorophenyl-2-nitrodiphenyl ether (FNDPE)	Tetrakis(trifluoromethyl)phenyl borate (KTTFMPB)
6	2-fluorophenyl-2-nitrodiphenyl ether (FNDPE)	chlorinated cobalt dicarbollide (CCD)
7	tris-(2-ethylhexyl) phosphate (TEHP)	Tetrakis(trifluoromethyl)phenyl borate (KTTFMPB)
8	tris-(2-ethylhexyl) phosphate (TEHP)	chlorinated cobalt dicarbollide (CCD)
9	bis(2-ethylhexyl) phthalate (DOP)	Tetrakis(trifluoromethyl)phenyl borate (KTTFMPB)
10	bis(2-ethylhexyl) phthalate (DOP)	chlorinated cobalt dicarbollide (CCD)