



Synthesis and application of tetrazole di- and triamide derivatives in ion-selective membrane electrodes



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ABSTRACT

A number of tetrazole diamides (**1–9**) and triamides (**10–11**) have been synthesized and applied as ion carriers in ion-selective membrane electrodes. Their selectivity and sensitivity were studied towards alkali, alkaline earth, transition and heavy metal cations. It was found that membranes doped with **3** and **2**-nitrophenyl octyl ether (*o*-NPOE) exhibit an almost theoretical Nernstian response for NH_4^+ over relatively wide concentration range. Electrodes with ionophores **4** and **5** with bis(1-butylpentyl)adipate (BBPA) show high affinity towards Cd^{2+} ; another diamide with two plasticizers exhibits good selectivity for Pb^{2+} ions. The best ionophores for Pb^{2+} ions proved to be tren-based triamides, having aryl groups substituted in *para* and *meta* position with tetrazole rings. They were suitable for use in aqueous solution in a wide range of pH 2–10 and had a fast response time $t_{95} < 20$ s. The electrode with ionophore **11** containing *o*-NPOE has a wide linear range and good selectivity for Pb^{2+} ions over Na^+ ions ($\log K_{\text{Pb,Na}} = -4.39$). The relation between the carrier structure and electrode properties has been discussed.

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1. Introduction

The development of new artificial receptors, chemical potentiometric sensors for transition metal ions is still very important due to their impact on human health and the environment. The ion-selective electrodes (ISEs) currently are one of the most important groups of chemical sensors. ISEs are used mainly to determine activities of Na^+ , K^+ , Cl^- , Ca^{2+} , Mg^{2+} and Li^+ ions in biological fluids [1,2]. Therefore, the design and synthesis of new selective carriers is significant for the ISE development and is central issues in modern chemistry. Potentiometric research uses simple and low-cost instrumentation, and the preparation of electrodes is very easy and not time consuming. In addition, the sample size is minimal and the research does not destroy it which is particularly important for the determination of environment (e.g. waste). At the present time, quantitative analysis of surface water and drinking water as well as monitoring industrial effluents requires design of new environmentally friendly, non-toxic and easy to obtain e.g., neutral carrier type ion-selective electrodes for detection of Pb^{2+} , Cd^{2+} , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , H^+ and Cu^{2+} ions [3]. For ions with single charge selectivity is achieved more easily, particularly with respect to double charge ions. Therefore, the use of ionophores in ion-selective electrodes for multivalent ions rarely gives positive results towards cations of

the first and second group because of their high concentration in the drinking water compared to low concentration of the examined ions.

Many compounds used as sensing ligands in new Cd^{2+} [4,5] and Pb^{2+} [6–8] ion-selective membrane electrodes have been reported. Nowadays the best commercially available ionophore selective for Pb^{2+} ions is amide derivative of substituted porphins which is sold as *lead ionophore VIII* [9], whereas for Cd^{2+} ions is derivative of oxa-dithioamides which is sold as *cadmium ionophore I* [9]. The selectivity coefficient of an electrode defines the ability of the ISE to distinguish the ion of interest from interfering ions. Hg^{2+} , Ag^+ and Cu^{2+} seriously interfere with Cd^{2+} and Pb^{2+} in ion-selective electrodes. ISEs based on amide [10] and thioamide derivatives [11] offer a reasonable discrimination of all alkali and alkaline earth metal ions but suffer from strong interference from Ag^+ and Cu^{2+} ions.

The development of analytical methods for the determination of NH_4^+ has various applications such as environmental control of waste waters. Accordingly, for recent research a number of highly selective sensors for NH_4^+ ion have been reported [12], but only few reports describe ligands able to properly discriminate alkali and alkaline earth ions. A commercial clinical analyser for detection of NH_4^+ using urease and antibiotics nonactin, and monactin was introduced in 1997 [13]. Nonactin was at first tested as ionophore for K^+ ion-selective electrodes. ISE measurements for NH_4^+ have been performed mainly in a commercially available mixture of 75% nonactin and 25% monactin [14].

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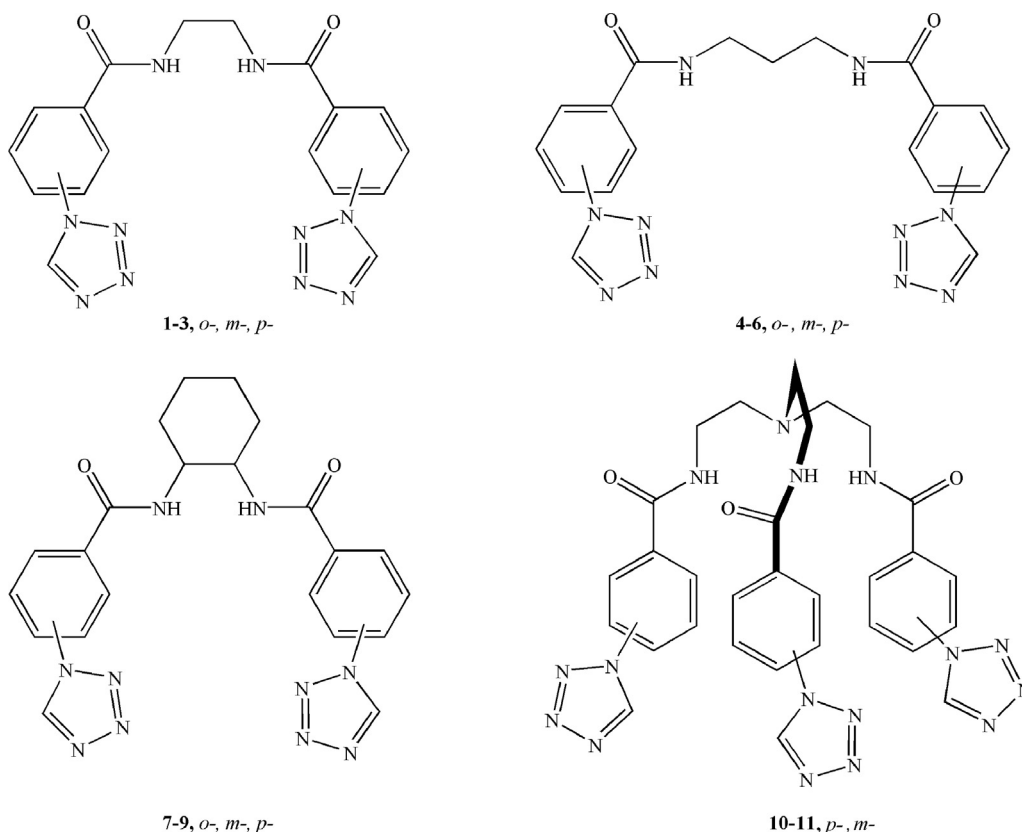


Fig. 1. Chemical structure of ionophores 1–11 used in ion-selective electrodes.

In our earlier paper we described that bis-(phenylhydrazono-1*H*-tetrazol-5-yl-acetonitriles) derivatives with different lengths of polyether chains are Pb^{2+} selective. Furthermore, the incorporation of sulphur and oxygen atoms into tetrazole podands improved Pb^{2+} selectivity ($\log K_{\text{Pb,Cu}} = -2$) [15].

The aim of this paper is detailed synthesis of tetrazole dipodal and tripodal ligands containing amide groups, and evaluation of the properties of 1–11 as cation carriers in membrane electrodes. Structures of the examined compounds are presented in Fig. 1. The behaviour of these compounds as ion carriers in ion-selective membrane electrodes has received no attention yet. According to our recent research, the biphenyl-based diamides derivatives of tetrazoles exhibit excellent anti-arthritis and anti-inflammatory activity than the reference drug diclofenac sodium [16]. The investigations were performed using human red blood cells membrane stabilization method.

2. Experimental

2.1. Reagents

Di- and triamide tetrazole derivatives 1–11 were synthesized according to procedure presented in Fig. 2. High molecular weight poly(vinyl chloride) (PVC), potassium tetrakis(*p*-chlorophenyl)borate (KTPCIPB) and tetrahydrofuran (THF), were purchased from Fluka. *o*-Nitrophenyl octyl ether (*o*-NPOE) and bis(1-butylpentyl) adipate (BBPA) as plasticizers were obtained from Sigma–Aldrich. All used reagents and solvents were of analytical reagent grade. Ethylenediamine, 1,3-diaminopropane, tris(2-aminoethyl)amine and diaminocyclohexane as mixture of *cis* and *trans* isomers were purchased from Sigma–Aldrich. Aqueous solutions were prepared from salts of the highest commercial

quality using deionized water (conductivity $\leq 0.03 \mu\text{S cm}^{-1}$), obtained from the HYDROLAB purification system.

Thin layer chromatography was done on aluminium plates covered with silica gel 60 F254 (Merck). ^1H NMR spectra were recorded on Varian instrument at 200 MHz. IR spectra in dry KBr were taken on Genesis II FT-IR (Mattson) instrument. Mass spectra were done on AutoSpec Premier (Waters) (EI) apparatus. The melting points are uncorrected.

2.2. General procedure for synthesis of substrates: (1*H*-tetrazol-1-yl)benzoic acids

Aminobenzoic acid (1.37 g, 10 mmol), sodium azide (1.56 g, 24 mmol) and triethyl orthoformate (4.98 ml, 30 mmol) were dissolved in 5 ml glacial acetic acid and the mixture was stirred at 80 °C for 5 h. Next the mixture was cooled to room temperature and poured into 50 ml of water and brought to pH 2 with concentrated HCl. The precipitate was filtered off and washed with: water (2×20 ml), 10% NaHCO_3 solution (2×20 ml), and water (3×20 ml).

2-(1*H*-tetrazol-1-yl)benzoic acid: White solid; mp 198–200 °C; 80% yield. ^1H NMR (200 MHz, *d*-DMSO): $\delta = 7.70\text{--}7.87$ (*m*, 3H, H_{Ar}), 8.09 (*dd*, $J_1 = 7.04$ Hz, $J_2 = 8.05$ Hz, 1H, H_{Ar}), 9.84 (*s*, 1H, CH), 13.4 (*s*, 1H, OH) ppm. IR(KBr): 3114, 2916, 2782, 2611, 2481, 1705, 1602, 1498, 1410, 1314, 1207, 1176, 1084, 1004, 969, 896, 801, 755, 689, 669, 640, 553, 533, 458 cm^{-1} . HRMS (EI) calcd. for $\text{C}_8\text{H}_6\text{N}_4\text{O}_2$: $m/z = 190.04908$, found: 190.04862.

3-(1*H*-tetrazol-1-yl)benzoic acid: White solid; mp 193–195 °C; 99% yield. ^1H NMR (200 MHz, *d*-DMSO): $\delta = 7.79$ (*t*, $J = 7.94$ Hz, 1H, H_{Ar}), 8.08–8.21 (*m*, 2H, H_{Ar}), 8.43 (*s*, 1H, H_{Ar}), 10.23 (*s*, 1H, CH), 13.5 (*s*, 1H, OH) ppm. IR(KBr): 3465, 3396, 3126, 3090, 2905, 2809, 2630, 2533, 1688, 1592, 1480, 1423, 1358, 1306, 1293, 1217, 1103, 1063,

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