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Ion-selective electrodes based on L-tryptophan and L-tyrosine

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ABSTRACT

Novel ion-selective electrodes (ISEs) based on amino acids have been developed. L-Tryptophan and L-tyrosine, which are amino acids, are employed as ionophores for solvent polymeric membrane electrodes. The proposed ISEs show rapid Nernstian responses for the Cu^{2+} ion over the concentration ranges of 3.0×10^{-4}–1.0×10^{-1} M. These ISEs exhibit comparatively good selectivity with respect to alkaline, alkaline earth, and some transition and heavy metal ions and the ammonium ion. The ISE based on tryptophan also indicates the Nernstian response for the benzylammonium ion.

1. Introduction

Ion-selective electrodes (ISEs) form one of the most important groups of chemical sensors. ISEs are sensitive towards a broader range of activities (concentrations) of analyte ions [1]. Solvent polymeric membrane electrodes are suitable devices for the development of ISEs having the diverse abilities of ion discriminations. A solvent polymeric membrane electrode is composed of an ionophore, a polymer, a plasticizer, and an additional salt. An ionophore really discriminates ions, which is dissolved or dispersed in a solvent polymeric membrane electrode. The original ion selectivity of an ionophore is directly reflected in the resulting ion-sensing behavior of the ISE. Numerous compounds such as crowns, calixarenes, and antibiotics, have been reported as ionophores for the cation-sensing [2,3].

Twenty-two amino acids are the building blocks of proteins and critical to life. The essential amino acids, which cannot be made by humans, are histidine, isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, and valine. Other 13 amino acids are called non-essential amino acids. In the field of analytical chemistry with ion-selective electrodes, the determinations of amino acids and the esters have been important and attractive issues [4–12]. Amino acids will be expected to act as functionalized molecules, for example, to discriminate specific ions, because they have an amino group and a carboxyl group in one molecule. In fact, the various interactions of amino acids with divalent metal ions such as Ca^{2+} [13], Cu^{2+} [14], Cd^{2+} [15], Hg^{2+} [16] have been reported. Only a few works, however, have reported the determinations of ions by ISEs incorporating improved derivatives with amino acids. The ISE based on the calix[4]arene arming with amino acid (Gly) ester unit was proposed by Kovalev et al. [17]. The NO_3^--selective electrodes based on N,N,N-triallyl α-amino acid (Gly) betain salts was presented by Scholefield et al. [18]. Nishino et al. demonstrated the Ca^{2+}-selective electrode based on the cyclic hexapeptide (Amy-Pro-Ala) [19].

Here, we propose novel solvent polymeric membrane electrodes incorporating amino acids as ionophores. Tryptophan and tyrosine, which are amino acids, behave as ionophores of solvent polymeric membrane electrodes. The proposed ISEs exhibit high sensitivity and selectivity for the Cu^{2+} ion over many common ions. To our knowledge, this is the first report on characterization of polymeric membrane electrodes based on amino acids as ionophores.

2. Experimental

2.1. Reagents

All chemicals were commercially available and used as such unless otherwise specified. Tetrahydrofuran (THF) was dried over sodium and distilled. Aqueous solutions were prepared with double quartz-distilled water and salts of the highest purity available. High-molecular-weight poly(vinyl chloride) (PVC) was twice purified in MeOH.

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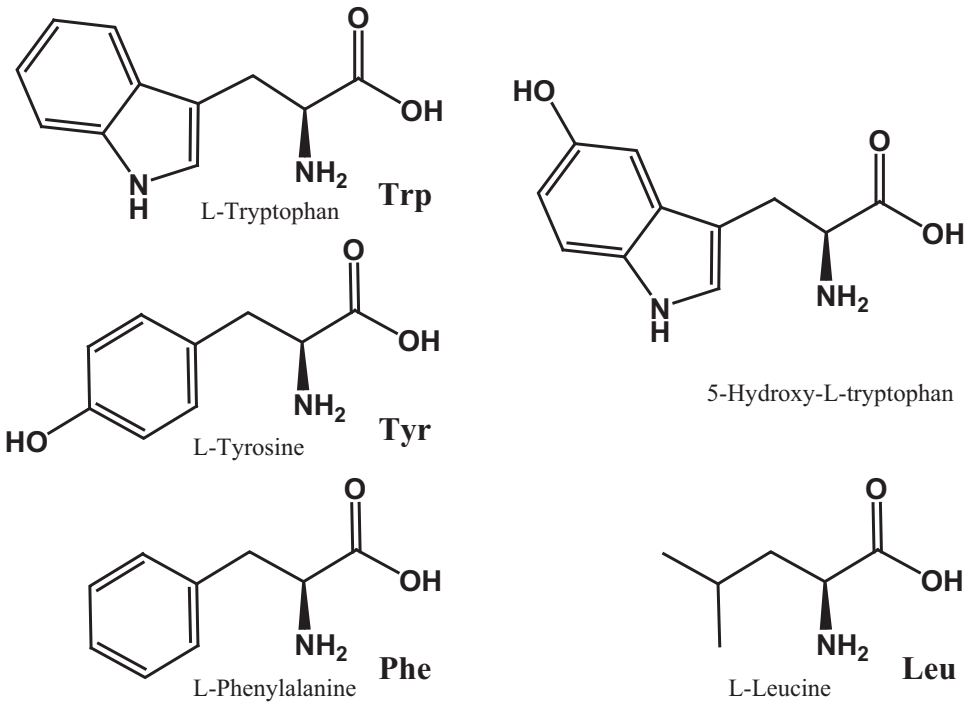

Fig. 1. Examined amino acids and the derivative.

2.2. Preparation of potentiometric liquid membranes

The composition of a potentiometric polymeric membrane incorporating an amino acid was 73.3 mg (27.4 wt%) of PVC as a polymer, 181.4 mg (67.7 wt%) of 2-nitrophenyl octyl ether (*o*-NPOE) as a membrane solvent, 13.0 mg (4.9 wt%) of an amino acid as an ionophore. The employed amino acids and the derivatives were L-tryptophan (Trp), L-tyrosine (Tyr), L-phenylalanine (Phe), L-leucine (Leu) and 5-hydroxy-L-tryptophan (Fig. 1). No anion excluder for the potentiometric cation-sensing membranes was employed. The components were put into a 5 mL of sample glass tube and dissolved in ca. 3 mL of THF. The potentiometric polymeric membrane was formed on the tip of the ISE body assembly with an electrode kit (DKK Co. Ltd., Tokyo) by a casting method. The obtained potentiometric polymeric membrane-based ISEs were then conditioned in an aqueous 0.01 M $CuCl_2$ (for Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} ions) or $Cu(NO_3)_2$ (for the Ag^+, Cd^{2+} and Pb^{2+} ions) solution overnight.

2.3. EMF measurement and selectivity factors

EMF measurements were performed on cells of the type Ag–AgCl|0.1 M $AgNO_3$||membrane||sample solution|0.1 M CH_3COOLi||3.3 M KCl|AgCl–Ag at $25 \pm 0.1\,^{\circ}C$ using a pH/mV meter equipped with a double junction type Ag–AgCl reference electrode. The activity coefficients were calculated according to the Davies equation [20]. EMF measurements of the solvent polymeric membrane electrodes were carried out in increasing Cu^{2+} concentration. The electrode potential was recorded as a function of the Cu^{2+} activity, giving the calibration plot (Fig. 2). The selectivity coefficients were determined by the matched potential method (MPM) [21] (Fig. 3). The Ca^{2+} ion was employed for the identical reference solution.

3. Results and discussion

An ionophore is dissolved or dispersed in the potentiometric polymeric membrane, really discriminating ions. An ionophore

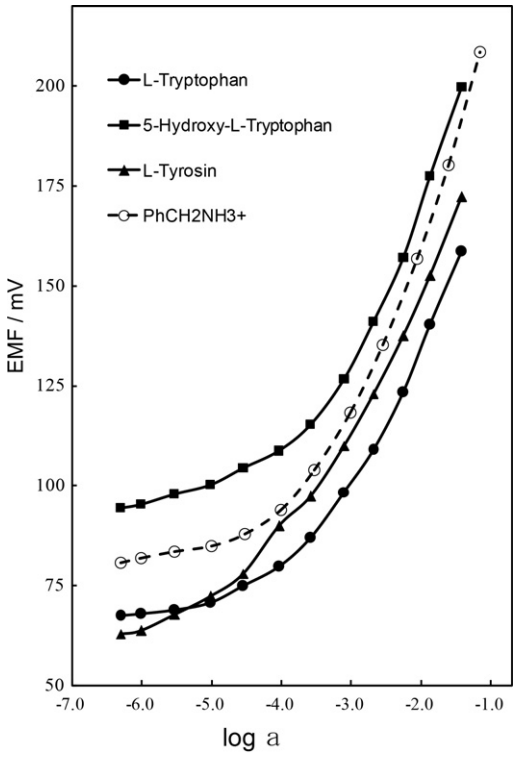

Fig. 2. EMF responses of solvent polymeric membrane electrodes based on amino acids and the derivative: (●) using tryptophan for Cu^{2+}, (■) using 5-hydroxy-tryptophan for Cu^{2+}, (▲) using tyrosine for Cu^{2+}, (○) using tryptophan for $PhCH_2NH_3^+$.