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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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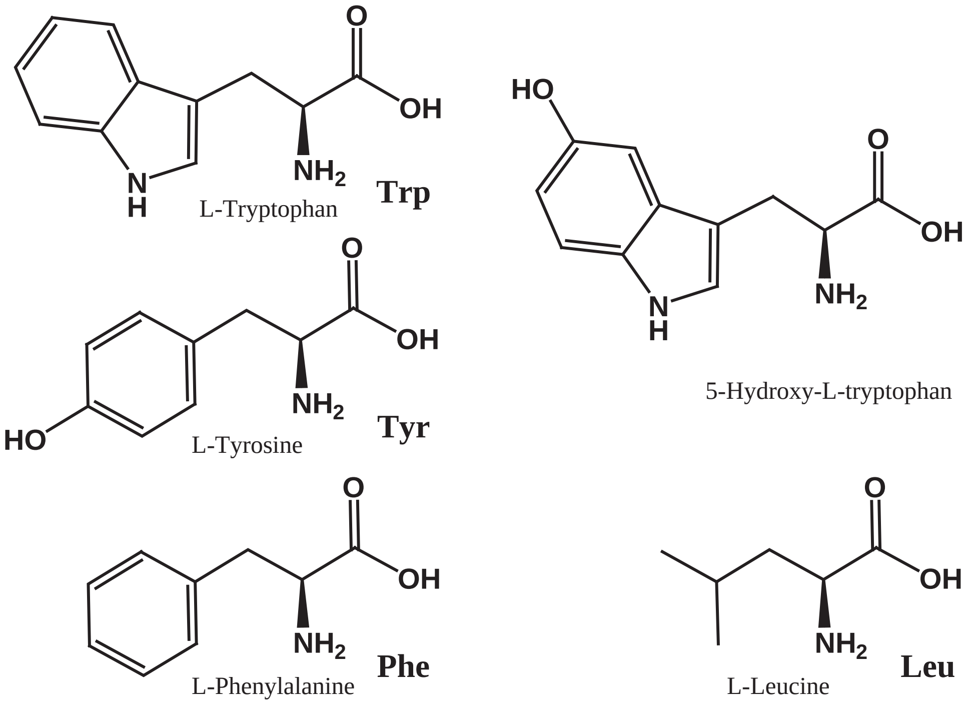

Fig. 1. Examined amino acids and the derivative.

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 ± 0.1 °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

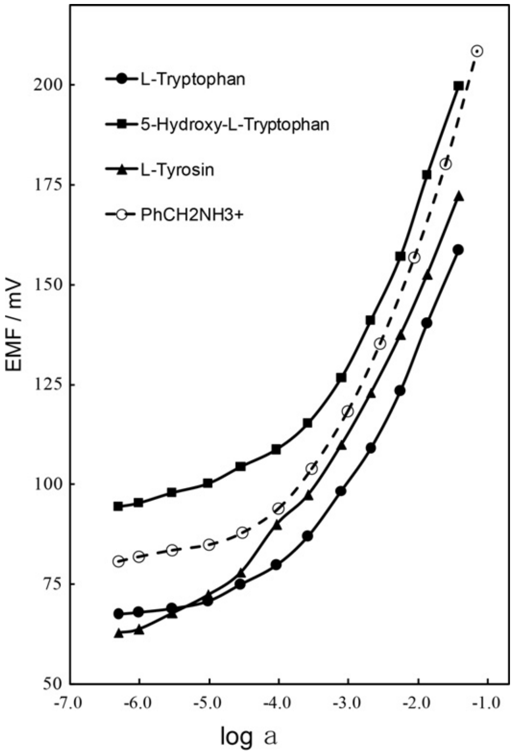

Fig. 2. EMF responses of solvent polymeric membrane electrodes based on amino acids and the derivative: (●) using tryptophan for Cu^{2+}, (■) using 5-hydroxy-tryptophan for Cu^{2+}, (▲) using tyrosine for Cu^{2+}, (○) using tryptophan for $PhCH_2NH_3^+$.

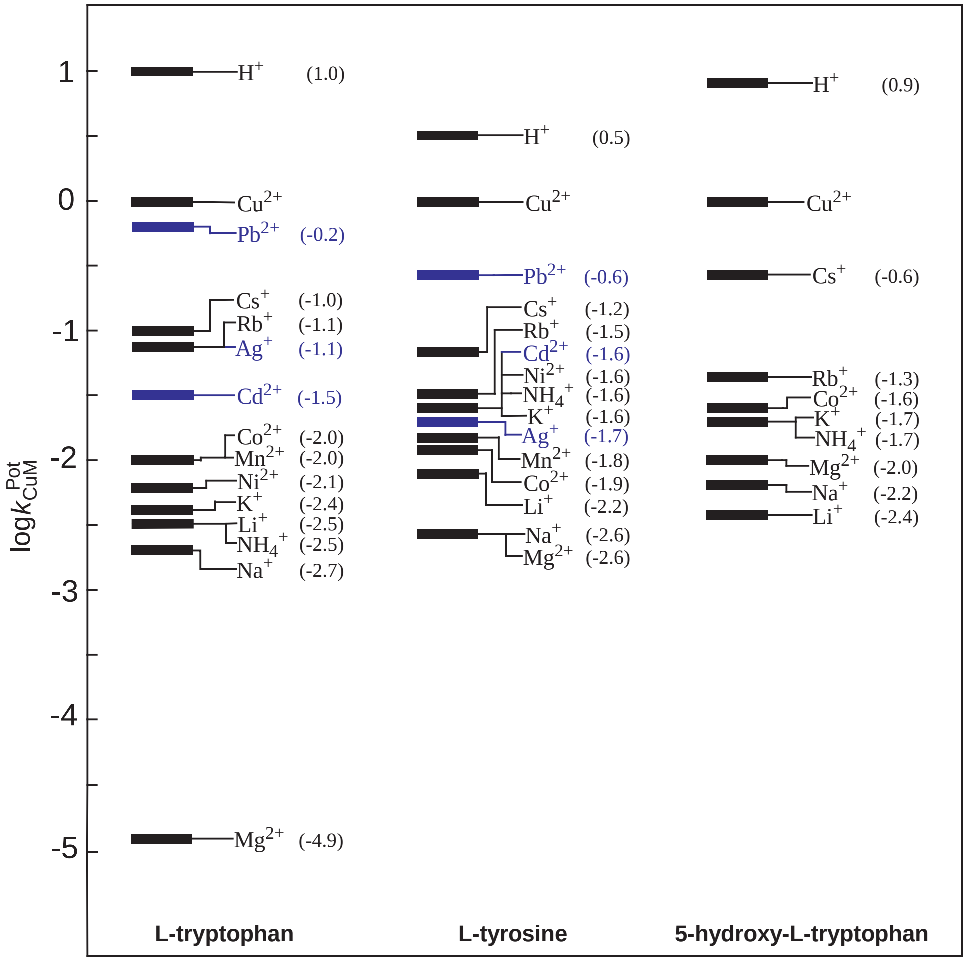

Fig. 3. Selectivity coefficients of potentiometric liquid membrane electrodes based on amino acids and the derivative (determined by the matched potential method (MPM)).

which is water-soluble will result in the instable ISE response due to effusion of an ionophore from the potentiometric polymeric membrane. Most amino acids are water-soluble and unsuitable for an ionophore of the ISE. To develop novel ISEs based on amino acids, we selected four amino acids as ionophores for metal ions: tryptophan, tyrosine, phenylalanine, and leucine illustrated in Fig. 1. Among amino acids, they are hardly soluble in water. Tryptophan, tyrosine and phenylalanine are aromatic amino acids and leucine is an aliphatic amino acid. Especially, tryptophan will be expected in discrimination of transition metal ions because of its pyrroline nitrogen atom. Four ISEs based on these amino acids as ionophores were prepared and investigated the potentiometric behaviors.

3.1. *Electrode performance*

In preliminary experiments, the ISE based on tryptophan as an ionophore was prepared. When the potential response to a 0.1 M solution of various ions was observed, respectively, the ISE based on tryptophan as an ionophore showed the selectivity for the Cu^{2+} ion. The Cu^{2+} ion is significant environmental pollutant and also an essential trace element in biological system [22]. In the field of analytical chemistry, the determination of the Cu^{2+} ion is important. Therefore, the ratio of membrane components, the conditioning solutions and concentration and time of conditioning solutions were optimized for the Cu^{2+}-selective potentiometric sensor. On the conditions, ISEs based on amino acids, tryptophan, tyrosine, phenylalanine, and leucine, as ionophores were prepared and examined.

The potential responses of four ISEs based on amino acids in the concentration range 5.0×10^{-7}–1.0×10^{-1} M solution of the Cu^{2+} ion are summarized in Table 1. ISEs based on tryptophan and tyrosine exhibited good Nernstian responses for the Cu^{2+} ion. For example, the ISE based on tryptophan displayed a linear response of the Cu^{2+} ion over the activity range of $10^{-3.6}$–$10^{-1.4}$ M with a detection limit $10^{-5.0}$ M and a calibration slope of 30.25 mV decade^{-1}. On the other hand, ISEs based on phenylalanine and leucine indicated no Nernstian responses for the Cu^{2+} ion. Tyrosine is an analog of phenylalanine attaching a OH group in *p*-position. In spite of structural similarity, the potential responses of ISEs based on tyrosine and phenylalanine were different for the Cu^{2+} ion. The ISE based on leucine indicated the lowest potential response for the Cu^{2+} ion. So we additionally selected 5-hydroxy-tryptophan as an ionophore for the Cu^{2+} ion. 5-Hydroxy-tryptophan which is not an amino acid is a derivative of tryptophan attaching a OH group. The ISE based on 5-hydroxy-tryptophan also exhibited a good Nernstian response for the Cu^{2+} ion. EMF responses of solvent polymeric membrane electrodes based on tryptophan, tyrosine and 5-hydroxy-tryptophan in the concentration range 5.0×10^{-7}–1.0×10^{-1} M solution containing the Cu^{2+} ion are illustrated in Fig. 2.

3.2. *Ion-selectivity*

ISEs based on tryptophan, tyrosine and 5-hydroxy-tryptophan exhibited Nernstian responses for the Cu^{2+} ion. The selectivity coefficients of the ISEs based on tryptophan, tyrosine and 5-hydroxy-tryptophan against series of ions were evaluated using

Table 1
Potential responses to Cu^{2+} activity changes for the solvent polymeric membrane electrodes based on amino acids and the derivative.

Ionophore	Calibration graph		
	Slope/mV decade^{-1}	Linear range/log $a_{Cu}{}^{2+}$	Detection limit/log $a_{Cu}{}^{2+}$
L-Tryptophan	30.3 (29.6)[a]	−3.6 to −1.4	−5.0
5-Hydroxy-L-tryptophan	30.7 (29.6)[a]	−3.6 to −1.4	−6.0
L-Tyrosine	29.7 (29.6)[a]	−3.6 to −1.4	−6.0
L-Phenylalanine	14.1 (29.6)[a]	−2.6 to −1.1	−6.3
L-Leucine	10.8 (29.6)[a]	−4.5 to −2.6	−6.3

[a] The ideal Nernstian slope.

the matched potential method (MPM). The selectivity coefficients against Li^+, Na^+, K^+, Rb^+, Cs^+, $NH_4{}^+$, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} ions were examined by using aqueous metal chloride solutions. Fig. 3 compares the selectivity coefficients of ISEs based on tryptophan, tyrosine and 5-hydroxy-tryptophan. No interference of the Zn^{2+} ion was observed on these ISEs. The ISE based on tryptophan recognized the Cu^{2+} ion as the primary ion reasonably well except the H^+ ion even when some other ion is present. The selectivity coefficient ($\log k^{\mathrm{Pot}}_{\mathrm{Cu,M}}$) values lie in the range of −1 to −5 for the metal ions indicating very good selectivity for the Cu^{2+} ion of the ISEs based on tryptophan. Likewise the ISE based on tyrosine indicated the Cu^{2+} ion-selectivity. As expected tryptophan discriminated various metal ions than tyrosine. As compared with those of the ISEs based on amino acids, the ion-selectivity of the ISE based on 5-hydroxy-tryptophan was a little inferior. The selectivity coefficients of ISEs based on amino acids against Ag^+, Cd^{2+} and Pb^{2+} ions were also examined by using aqueous metal nitrates solutions. Tryptophan might strongly interact with metal ions by its pyrroline nitrogen and the ISE based on tryptophan exhibited comparatively high selectivity for the Pb^{2+} and Ag^+ ions. Although the interference of the Ag^+ ion was improved compared to established solid-state electrodes based on $CuS–Ag_2S$ [2], the proposed ISEs have no advantage in the selectivity over the previously reported solvent polymeric electrodes based on neutral carriers [23,24]. However, the proposed ISEs are suitable for the facile determination of the Cu^{2+} ion because tryptophan and tyrosine are commercially available and inexpensive.

3.3. *The pH dependence*

Amino acids are amphoteric electrolytes, being dissociated into various ionic species depending on pH, and are dissociated in solution into various ionic species such as bivalent anion A^{2-}, monovalent anion A^-, and bivalent cation A^{2+} [25]. Despite a lack of water-solubility, the serious interference by the H^+ ion was observed on ISEs incorporating tryptophan and tyrosine, as shown in Fig. 3. Hence, the pH dependence of response of the ISE based on tryptophan was examined by using the 0.1 M Cu^{2+} solution. The adjustment of pH was performed using dilute HCl and NaOH aqueous solutions. The pH of the solutions was varied in the range 1.0–7.0. The influence of the pH on the EMF response is illustrated in Fig. 4. As seen, stable response over the pH range 4.6–7.0 was obtained. At low pH, the interference of the H^+ ion may be due to the high rate of diffusion of the H^+ ion from the sample solution to the potentiometric membrane where the H^+ ion interacts with an ionophore and protonates of the nitrogen atom, decreasing its selectivity to the Cu^{2+} ion. At high pH, the deviation in the EMF response is probably due to the hydrolysis of the Cu^{2+} ion by NaOH providing the white precipitate. Tryptophan is an amino acid with pK_a values of 2.36 ($—COO^-$ group) and 9.42 ($—NH_3{}^+$ group) [26]. Therefore, tryptophan would act as an neutral carrier for the ISE over the pH range 4.6–7.0.

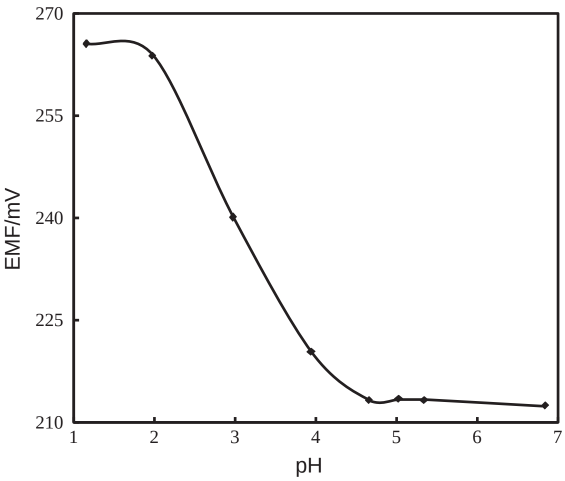

Fig. 4. Effect of the pH on the potential responses of the potentiometric liquid membrane electrode based on tryptophan.

3.4. *Response for benzylammonium ion*

The ISE based on tryptophan can be employed for rapid determination of benzylammonium ion $PhCH_2NH_3{}^+$. The EMF response of solvent polymeric membrane electrodes based on tryptophan in the concentration range 5.0×10^{-7}–1.0×10^{-1} M solution containing the $PhCH_2NH_3{}^+$ ion are illustrated in Fig. 2. The ISE based on tryptophan displayed a linear response of the $PhCH_2NH_3{}^+$ ion over the activity range of $10^{-3.0}$–$10^{-1.2}$ M with a detection limit $10^{-5.5}$ M and a calibration slope of 57.42 mV decade^{-1}. Moreover, the selectivity coefficient ($\log k^{\mathrm{Pot}}_{\mathrm{Cu,M}}$) of the Cu^{2+} ion against the $PhCH_2NH_3{}^+$ ion was −0.76. Because the selectivity coefficient ($\log k^{\mathrm{Pot}}_{\mathrm{Cu,M}}$) of the Cu^{2+} ion against the $NH_4{}^+$ ion was −2.5, the ISE based on tryptophan would discriminate the $PhCH_2NH_3{}^+$ ion from the $NH_4{}^+$ ion.

4. Conclusion

Novel ISEs based on amino acids, tryptophan and tyrosine, were proposed. The ISEs based on amino acids exhibited the good potentiometric responses and the comparatively good selectivities for the Cu^{2+} ion. The ISE based on tryptophan can be employed for determination of the $PhCH_2NH_3{}^+$ ion. The ISE based on tryptophan also indicates the Nernstian response and the high discrimination for the $PhCH_2NH_3{}^+$ ion.

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