

Synthesis of Poly(Benzyl-eugenol) and Its Application as an Ionophore for a Potassium Ion-Selective Electrode

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Poly(benzyl eugenol)(PBE) as novel ionophores for a K^+ ion selective electrode was synthesized by acid catalyzed polymerization of benzyl eugenol. The polymerization product was characterized by IR and 1H NMR. The electrode membranes based on the polymer were prepared in the composition of 3 wt% of PBE, (67-n) wt% of 2-nitrophenyl octyl ether (o-NPOE) as a membrane plasticizer, n wt% of oleic acid as a lipophilic anionic additive (which n were varied from 0-10) and 30 wt% of PVC as a membrane matrix. Each membrane electrode was characterized for their performance as an ion-selective electrode membrane, that was selectivity, Nernst factor, limit of detection (l.o.d.), response time, and lifetime. Experimental results showed that the electrode membrane based on PBE with 3 wt% of oleic acid exhibited the best selectivity for K^+ ion relative to other alkali and alkali earth metal ion. The K^+ -ISE based on PBE with the membrane composition of 3 wt% PBE, 3 wt% oleic acid, 64 wt% o-NPOE and 30 wt% PVC exhibited potentiometric selectivity toward NH_4^+ , Na^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} and Al^{3+} of -0.6; -1.3; -3.2; -2.5, -2.2 and -2.5; respectively. This electrode gave a sub-Nernstian response with a slope of 56.3 mV/decade; the response time of c.a. 30 s; the dynamic range of 10^{-4} – 10^{-1} M and limit of detection of $10^{-4.7}$ M. The electrode may be used for continuous measurement at least up to two weeks.

Keywords: poly benzyl eugenol, ion-selective electrode, potassium ion, oleic acid

INTRODUCTION

Ion-selective electrode (ISE) is one widely used analytical method, especially for routine analysis in environmental monitoring, control in the industrial process, clinical analysis and biochemical analysis. The advantages of the use of ISE for routine analysis are its high selectivity, fast response time, relatively low cost, and high sensitivity and accuracy. Therefore, the development and application of highly selective ISE tend to increase in the last decade [1–5].

The history of ISE begins in 1900 when Haber and Clemensiewicz successfully

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developed a glass electrode that produced an electrochemical signal as a response to the acidity of an aqueous solution [6]. This finding then contributed to the definition of pH and for the development of a glass electrode for measurement of the pH of an aqueous solution. Using the same model, Eisenmann successfully developed other glass electrodes for measurement of Na^+ , K^+ , Ag^+ , NH_4^+ , Ti^+ , Li^+ and Cs^+ employing different type glass material of specific composition as the sensor element. A significant progress took place after Pedersen found crown ethers as a new type of molecules that could form a stable complex to alkali and alkaline earth metal ions [7]. This new type of compound then found its high popularity to be used as ionophores for that class of ion.

Various types of ionophore for the electrode membrane was reported, such as various derivatives of the crown ether, polyether amide, and calixarene. In general, the ionophores should contain donor atoms such as oxygen, nitrogen, and sulfur, and arrange in such as the molecular structure that could bind coordinatively to a metal ion. In this case, general principle of Hard Soft Acid and Base (HSAB), that hard acid will bind strongly hard base and vice versa, could be used as general guidance for selecting better ionophore for specific cation. Therefore, an ionophore that contains nitrogen or sulfur atom will form stable complexes to transition metal ions, especially to soft metal ion such as Ag^+ [8, 9]; Hg^{2+} [10–12] and Pb^{2+} [5, 13–17].

The availability of highly selective ionophores as an essential component in an ion-selective electrode membrane is very crucial. Therefore, many works have been reported on the synthesis of new ionophores to improve the selectivity and sensitivity of an ion-selective electrode for Bi^{3+} [18]; Cs^+ [19]; Tl^+ [20]; $[\text{Pb}^{2+}$ [21]; Zn^{2+} [22]; Cd^{2+} [23]; Co^{2+} [24]; Cu^{2+} [25, 26]; Hg^{2+} [27]; Ce^{3+} [28]; anion [29]. In most cases, the preparation of highly selective ionophores for commercial purposes is comparatively very expensive and requires many reaction steps. In this work, we introduce a polymeric ionophore as a new type of ionophoric compound, which is relatively easy to be synthesized. By using this type of compound, we could prepared an ISE with a reasonable selectivity, but high stability as this ionophore should have high lipophilicity. Poly(benzyl eugenol) which synthesized from benzyl eugenol monomer, which has two ethereal oxygens in each monomer, may form a "polar tunnel" in the electrode membrane as a track for transporting ions through the membrane.

EXPERIMENTAL

Reagents

The highest grade commercially available reagents were used for synthesis on new compound and preparation of the aqueous test electrolytes. The distilled deionized water was for preparation of an aqueous solution. The membrane solvent 2-nitrophenyl octyl ether (o-NPOE) was purchased from Dojin Laboratory (Kumamoto, Japan). Poly(vinyl chloride) (PVC, high molecular weight type) used as the electrode membrane matrix was obtained from Sigma Chemical Co. (St. Louis, MO).

Synthesis of Poly(Benzyleugenol) (PBE)

Synthesis of PBE was conducted in two steps, i.e. synthesis of benzyl eugenol from eugenol and polymerization of benzyl eugenol into PBE.

Synthesis of Benzyl Eugenol

Eugenol (2-methoxy-4-allyl phenol, 10 g, 63 mmol) was placed in a 250 mL three neck flask and subsequently KOH (4 g) and water (10 mL). After heating the solution,

benzyl chloride (9 g, 71 mmol) was afterward added into the mixture slowly in 10 min. The reaction mixture was refluxed for 3 h and then extracted using dichloromethane (3 × 50 mL) and washed the organic phase using 0.5 M KOH (3 × 30 mL), subsequently washed with water until neutral. The organic phase was dried using anhydrous sodium sulfate and evaporate to obtain the residue as benzyl eugenol as a liquid.

Polymerization of benzyl eugenol

Benzyleugenol (2.00 g, 7.9 mmol) dissolved in 25 mL of n-hexane in a 250 mL three neck flask under nitrogen atmosphere. Then 0.2 mL (3.7 mmol) concentrated H₂SO₄ was introduced into the reaction and stirred for two hours, and the solid polymer was formed. Methanol (1 mL) was added to the reaction mixture to terminate the polymerization reaction. The precipitate was separated from the solution, dissolved in 25 mL of chloroform, washed with distilled water until neutral, then the solvent was evaporated. The polymers were analyzed by a spectrometer ¹H NMR and IR spectrometer.

Preparation of test solution

The test solution was prepared by dissolving a weighed amount of chloride salt of potassium, ammonium, sodium, calcium, barium, magnesium, nickel, lead and zinc to make a 0.1 M solution. For preparing calibration curve, KCl solution of various concentrations in the range of 10⁻² M – 10⁻⁷ M was prepared by dilution of 0.1 M KCl solution.

Preparation of electrode membrane for measurement of cell potential (emf)

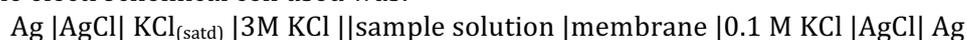
Polymer liquid membrane by mixing ionophore (PBE), plasticizer (o-NPOE), PVC, and oleic acid in specific composition and total mass 150 mg. Membrane composition are shown in Table 1. The chemical structures of the membrane components are shown in Figure 1.

Table 1 Membrane compositions examined in this experiment.

Membrane	PBE (wt%)	Plasticizer (o-NPOE) (wt%)	Oleic acid (wt%)	PVC (wt%)
I	3	67	-	30
II	3	66	1	30
III	3	64	3	30
IV	3	62	5	30
V	3	60	7	30
VI	3	57	10	30

The THF (3 mL) solution of the membrane component was put into a glass bottle with an inner diameter of c.a. 15 mm. Afterward, the solution will vaporize at room temperature for about 24 hours. Membrane sheet formed subsequently cut to be fit in the electrode mounting (diameter ± 12 mm). The membrane after that set into the electrode body and filled with the inner solution. The electrode was subsequently immersed in a 0.1 M KCl for more than 24 hours for conditioning before measurement.

The electrochemical cell used was:



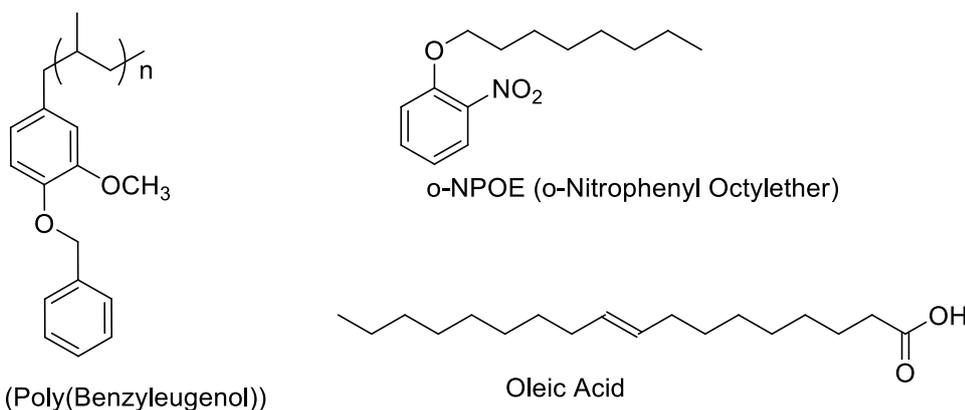


Figure 1 Chemical structures of the membrane components PBE, o-NPOE and oleic acid.

Characterization of the ISE

Potentiometric Selectivity Coefficients

Potentiometric selectivity coefficients determined according to IUPAC recommendations is by using the separate solution method (separate solution method, SSM).[30] Cell potential for primary ions (K^+) and interfering ions (NH_4^+ , Na^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , and Al^{3+}) is measured at the same concentration of 0.1 M.

Nernst factor

To determine the value of the Nernst factor is done by making a series of solutions of potassium and ammonium chloride at a concentration range of 10^{-7} – 10^{-1} M. Then each of the series solutions is measured cell potential (emf) with a membrane which shows selectivity towards potassium and ammonium. From the data obtained made cell potential curves (emf) versus the logarithm of the concentration of each of the major ions. ESI Nernst factor is determined from the slope of the curve that gives the highest linearity.

Response Time

To determine the length of time required ESI to achieve a steady response, measured cell potential (emf) of the test solution with a concentration variation in the linear region (10^{-4} – 10^{-1} M), each interval of five seconds to obtain a stable potential. This measurement is carried out for all the membranes are made.

Life Time

ESI lifetimes determined by measuring the cell potential (emf) of the test solution of potassium and ammonium chloride at a concentration range of 10^{-7} – 10^{-1} M in a variety of times (days). Age of the Nernst factor is determined based on the value obtained from the measurements as a function of time in days. Measurement was stopped when the Nernst factor of the membrane has deviated from the Nernst factor ESI.

RESULT AND DISCUSSION

Characterization of Benzyl Eugenol and PBE.

IR spectrum of benzyl eugenol showed absorption peaks at 2906 and 2839 cm^{-1} , supported with absorption peaks at 1454 and 1381 cm^{-1} , as the absorption peaks of

-CH₃ and -CH₂- group in the compound. Peaks at 3100 and 1591 cm⁻¹ exhibited the existence of aromatic benzene in the compound. C=C of the allylic group could be observed at 1637 cm⁻¹; while absorption peaks of C-O-C ether were observed at 1261 and 1033 cm⁻¹. ¹H NMR (Jeol MY60; 60 MHz) spectrum showed seven peaks: δ (ppm to TMS) 7.25-7.50 (5H, s); 6.60-7.00 (3H, m); 5.70-6.50 (1H, m); 4.80-5.20 (2H, m); 4.50 (2H, s); 3.50-3.90 (2H, m); 3.20-3.50 (3H, m). These spectroscopic data confirmed the chemical structure of benzyl eugenol.

IR spectrum of PBE compared to the spectrum of benzyl eugenol showed the disappearance of an absorption peak at 1637 cm⁻¹ as the evidence of vanishing of allylic C=C because its involvement in the polymerization reaction. This spectrum was supported by the ¹H NMR of PBE that did not exhibit peaks at 5.0 – 6.0 of the vinylic proton (-CH=CH₂). Therefore, we could conclude that PBE had been successfully synthesized.

Characterization of Potassium ISE

Selectivity Coefficients

Selectivity coefficient is an important parameter that determines the quality of an ISE. Selectivity coefficient gave a preliminary description of the strength of ion-ionophore association in the electrode membrane. The membrane based on newly synthesized PBE exhibited the highest potentiometric response to K⁺ comparative to the other ions, NH₄⁺, Na⁺, Ba²⁺, Al³⁺, Ca²⁺, and Mg²⁺ studied in this work. Cell potential data from each ion were then used to determine the value of potentiometric potassium ion selectivity (i, primary ion) relative to the interfering ions (j). In this study, we used SSM to determine the potentiometric selectivity coefficient, as the separate solution method (SSM) is simple, efficient and widely used. Potentiometric selectivity coefficient values (log K_{ij}^{pot}) for K⁺ of the electrode based on PBE was shown in Figure 2.

The composition of the membrane I-VI consists of ionophores (3% PBE), plasticizer (o-NPOE), additives (oleic acid) and PVC matrix (30%). The difference lies in the amount of oleic acid were added, respectively, for membranes I-VI are as many as 0, 1, 3, 5, 7 and 10%. For each addition of oleic acid followed by reduction of the amount of plasticizer in the membrane, so the total weight of the membrane remained the same (150 mg). This variation is made to obtain the optimization results of ESI selectivity in potassium. Previous investigators using oleic acid as an additive in the ESI Pb²⁺[31], ESI Cu²⁺ [32], ESI Hg²⁺[33]. From the measurement results, the best selectivity coefficient indicated by the membrane III (3% oleic acid). This means that the membrane III has the finest ability to distinguish potassium ions in the presence of other interfering ions.

The addition of oleic acid as a membrane additive provides a significant increase in selectivity. The electrode based on membrane I (without oleic acid as a lipophilic anionic site in the organic membrane phase) gave the worst response in comparison to the other membrane and showed no ionic selectivity to all ions tested. This fact confirms the function of a lipophilic anionic site in the membrane to facilitate the transfer of cation into the organic membrane phase, to keep the electric neutrality of the membrane and to prevent co-transport of anion from aqueous solution (anionic interference).[34] The addition of lipophilic anions in the membrane II-VI helps the cations' transport through the membrane so that the electrode response was improved. As the result, the electrode based on membrane II – VI exhibited improved ionic selectivity. However, excessive addition of an oleic acid can also cause drastic changes in the selectivity of the membrane as shown by K⁺-selectivity of the membrane IV, V, and VI. The addition of more oleic acid additives may actually

lower the potentiometric selectivity of the membrane. If the anionic additive presents in higher concentration, then a competitive interaction between unselective anionic-cationic species interaction and selective cationic species-neutral ionophore interaction would happen. The experiment showed that 3 wt% of PBE and 3 wt% oleic acid in the membrane gave the K⁺-selectivity to other interfering ions.

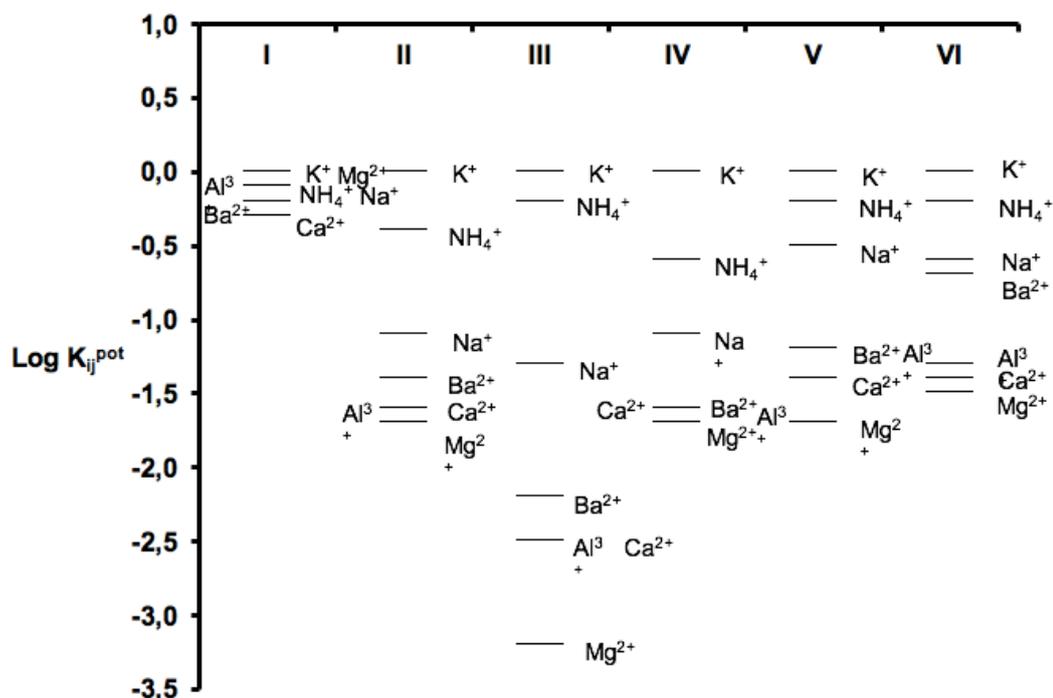


Figure 2 Selectivity coefficients ($\log K_{ij}^{pot}$, $i = K^+$, $j =$ interfering ions) of the electrodes based on the ionophore PBE. For electrode membrane composition see Table 1.

Nernst factor

Nernst factor indicates the sensitivity of the potassium ion selective electrode and is an important parameter to determine the quality of an ISE [30]. Nernst factor is obtained by plotting the measured cell potential (emf) of various potassium ion concentrations against the logarithm of ion activity (a). Nernst factor is the slope of linear part (dynamic range) of the curve. The Nernst factor, dynamic range, limit of detection of the K⁺-ISE based on membrane I to VI presented in Table 2 and Figure 3.

Table 2 PBE-based K⁺-ISEs characteristics on the variation of wt% of oleic acid as a lipophilic anionic additive.

Membrane	Nernst Factor	Dynamic range (M)	Limit of detection (M)	Response time (s)	Lifetime (days)
I	13,2	10 ⁻⁴ – 10 ⁻¹	10 ^{-4,3}	150	-
II	52,3	10 ⁻⁴ – 10 ⁻¹	10 ^{-4,7}	90	5
III	56,3	10 ⁻⁴ – 10 ⁻¹	10 ^{-4,7}	30	14
IV	48,9	10 ⁻⁴ – 10 ⁻¹	10 ^{-4,7}	75	5
V	48,8	10 ⁻⁴ – 10 ⁻¹	10 ^{-4,7}	75	5
VI	46,0	10 ⁻⁴ – 10 ⁻¹	10 ^{-4,6}	110	5

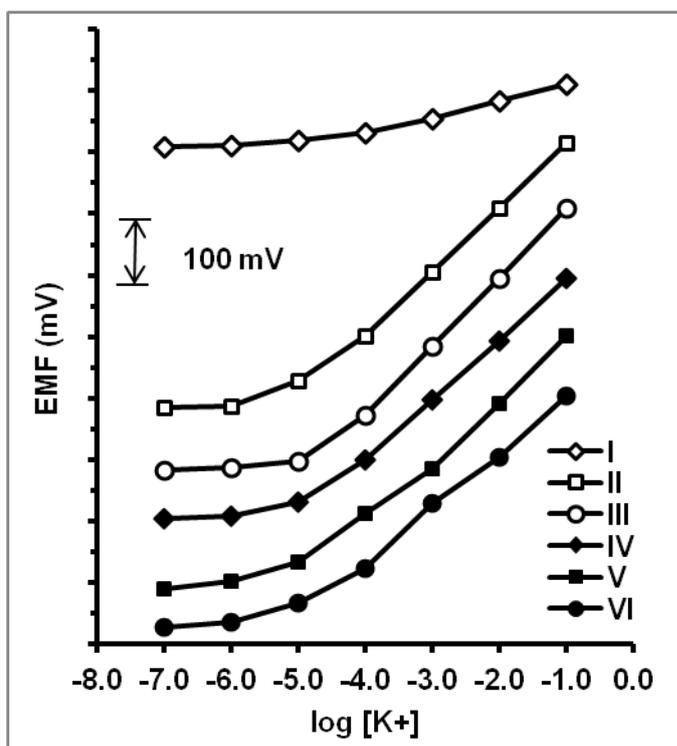


Figure 3 Response curves obtained with the electrode based on ionophore PBE. For electrode membrane composition, see Table 1.

Nernst factor value, as shown in Table 2, varies depending on the type of membrane. The addition of oleic acid on membrane II-VI of the membrane composition I (without oleic acid) will increase to K^+ -ISE Nernst factor of 13.2 mV/decade to 52.3; 56.3; 48.9: 48.8 and 46 mV/decade respectively for the ISE based on membrane II, III, IV, V and VI. It is clear here that the presence of the oleic acid as an anionic lipophilic additive in the membrane is very crucial to catalyzing the transfer of the cation from aqueous solution into lipophilic membrane phase. The addition of the lipophilic anionic sites increase the cation permselectivity of ionophore [35]. With the oleate ion in the membrane, the stability of the complex K^+ with the ionophore in the membrane will increase, thus Nernst factor for The K^+ -ISE based on PBE will also rise. Again, excessive addition of oleic acid (membrane IV-VI) may cause competitive interaction with PBE; which yield in lower Nernst factor in membrane IV-VI.

The best Nernst factor value is given by the K^+ -ISE base on membrane III that is 56.3 mV/decade. This electrode exhibited a slope that close to the theoretical value of Nernst factor (59.2 mV/decade). Nernst factor value also reinforces the selectivity results obtained, that the optimal conditions for the potentiometric membrane are produced through the addition of oleic acid into the membrane as much as 3%. Within this amount, oleic acid can effectively give rise to the selectivity and sensitivity of the K^+ -ISE, especially to Na^+ and alkaline earth metal ions.

Response Time

Response time measurements of an ISE are intended to determine the promptness of the stable response of a membrane to specific ions. The lower the ISE response time, the better the quality of the ISE. Fast response to a specific analyte ion is a measure of the efficiency of the ISE usage, which is an important parameter, especially for the routine analysis (Morf and Simon, 1981). Response time of K^+ -ISEs based on membranes I - VI are presented in Table 2.

Table 2 shows that the membrane I (without oleic acid) exhibited the longest response time to K^+ , which is in the order of 2.5 minutes. In contrast, other membranes showed a response time in the order of 0.5 – 1.5 minutes. Clearly the absence of oleic acid affect the permeability of the membrane that slowing down the response (Morf and Simon, 1981). The effects of addition of oleic acid into the membrane obviously accelerate the transport of the cation into the membrane of the ISE. Improved response time occurs in the membranes which with oleic acid were added to the membrane (membrane II-VI). Fastest response time is given by the K^+ -ISE based on membrane III (3% oleic acid) that is c.a. 30 s. This means that the addition of as much as 3% oleic acid into the membrane provides the most responsive K^+ -ISE.

Life Time

The lifetime of an ISE determines the economic aspect of the electrode usage. The lifetime of an ISE can be determined by evaluating periodically the Nernst factor of the electrode. If the electrode membrane were deteriorated, then the Nernst factor may decrease far from the theoretical value of 59.2 mV/decade. However, in practice Nernst factor value of 45 mV / decade is still acceptable. Thus, an ISE could not be used again if the Nernst factor of the membrane has deviated far from the theoretical Nernst factor. Nernst factor of K^+ -ISEs based on membrane II-VI measured at various time intervals (days) are presented in Table 2.

Table 2 shows that the Nernst factor for each ISEs decline with time. If we accept the lowest Nernst factor value of 45 mV/decade as the criteria for the ISE usability, then we can expect that the K^+ -ISE based on membrane III (3 wt% of oleic acid) has the longest lifetime, c.a. two weeks. In contrast, other ISEs could only be used for continuous measurement as long as a week. This result is still under the expectation as for practical usage an ISE should have lifetime at least for six months uninterrupted measurement. Deterioration of the electrode membrane may be caused by the leaching of the membrane component into the aqueous solution. In this case, membrane solvent (o-NPOE) and oleic acid has bigger tendency to leak to the aqueous solution rather than PBE, as PBE is a long-chain polymer that should have higher lipophilicity.

CONCLUSION

The result of the investigation gives an insight that a long chain polymeric compound such as poly(benzyl eugenol) (PBE) could perform as an effective ionophore for transporting cation through an ion-selective membrane. Of course, the ion transport mechanism may differ to the membrane based on simple molecules, such as valinomycin, crown ethers, calyx[4]arene derivatives, etc. In the conventional ionophores; we theorize that the cation-ionophore complex (association) is actively transported through the membrane using the driving force of a concentration gradient between the opposite sides of the membrane. In the polymeric ionophores, such mechanism may be difficult to be realized. Therefore, we expect that the cation may be transported through the membrane by a "polar tunnel" created by a regular arrangement of electron donating groups in each monomer of the polymer. The ions are handed over from one active site to the neighboring active site continuously through the membrane. This mechanism is reasonable as the membrane based on PBE exhibited a relatively fast response time comparable to the response time of the ISE based on conventional ionophores.

The K^+ -ISE based on PBE with the membrane composition of 3 wt% PBE, 3 wt% oleic acid, 64 wt% o-NPOE and 30 wt% PVC exhibited potentiometric selectivity toward NH_4^+ , Na^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} and Al^{3+} of -0.6; -1.3; -3.2; -2.5, -2.2 and -2.5;

respectively. This electrode gave a sub-Nernstian response with a slope of 56.3 mV/decade; dynamic range of 10^{-4} – 10^{-1} M and limit of detection of $10^{-4.7}$ M. The electrode may be used for continuous measurement at least up to 2 weeks.

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