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Potentiometric Cr(VI) selective electrode based on novel ionophore-immobilized PVC membranes

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Abstract

For the determination of Cr(VI) concentrations with a potentiometric ion-selective electrode (ISE), ionophore-immobilized membranes were prepared by ultraviolet (UV)-induced graft polymerization followed by chemical treatment. Novel ionophores comprising various amine structures were immobilized onto poly(vinyl chloride) (PVC) matrixes, and these were examined to determine Cr(VI) selectively. Of the three ionophores examined in this study, the membranes with *N*,*N*,*N*,*N*-tetrakis(3-aminopropyl)-1,4-butanediamine (DABAm4) exhibited the highest Cr(VI) ion selectivity in both extraction and potentiometry experiments. The plasticizer in the membrane was optimized as 1.0 ml *o*-nitrophenyl octyl ether (NPOE)/g PVC to form diffusible channels. The potentiometric studies revealed that the performance of DABAm4-immobilized PVC was equivalent to that of mobile ionophores in supported liquid membranes (SLMs). A reproducible response of Cr(VI) was attained within a response time of 1 s in the range of 2.16×10^{-6} to 0.1 M, using the membrane prepared in this study. The selectivity for the Cr(VI) ion against the other interfering ions was compared reasonably between a solvent extraction and potentiometry. The long-term response of the Cr(VI) ISE showed slight deterioration over a continuous operation for 6 months, while the detection limit slightly decreased due to the leaching-out of the plasticizer. The ISE along with the DABAm4 immobilized membrane showed a higher Cr(VI) ion selectivity and more stable response under long-term usage than ISEs with typical SLMs.

Keywords: Ionophore-immobilized membrane; Hexavalent chromate; Ion-selective electrode; Selectivity; Response stability

1. Introduction

Cr(VI) is one of several hazardous heavy metals monitored in water and wastewater streams. Ion-selective electrodes (ISEs) for Cr(VI) have been widely used with polymeric membranes containing appropriate carriers (i.e., the ionophore) [1–5]. In previous studies, supported liquid membranes (SLMs) were employed for the selective determination of Cr(VI). The SLMs that have been applied as Cr(VI) ISEs contain various electroactive ionophores, such as trioctyl amine [1], tetrakis (thiocyanato) chromate [2], diphenyl carbazide (DPC) [3], trioctyl phosphate (TOPO) [4], and tricaprylmethyl ammonium chloride (Aliquat336) [5]. These ionophores have been examined so that they could be incorporated to form complexes with Cr(VI) within the membrane. However, the electrodes still have some serious drawbacks, such as a short lifetime and an unstable response. Also, the leaching-out of the substances (ionophores and plasticizers) into the sample solutions further decreases the performance of the electrodes during a long term measurement of Cr(VI).

The most common ISEs require a polymeric ion-selective membrane containing ionophores. Usually poly(vinyl chloride) (PVC) and polymers based on silicon rubber and polyurethane have been used as matrix. A typical membrane composition for a PVC ion-selective membrane is

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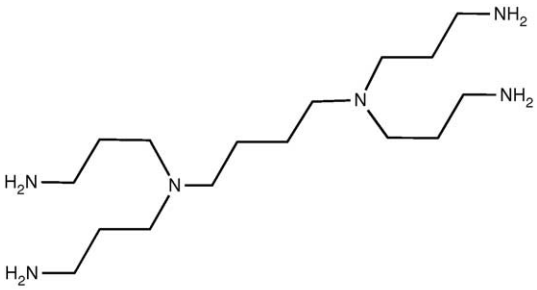
Nomenclature

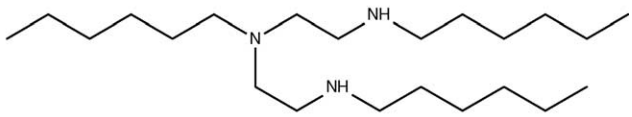
a_1	the activity of the primary ion
a_i	the activity of an interfering ion
E	the measured potential for the mixed ions
E_0	the standard potential
F	the Faraday constant
k_d	distribution coefficient
K_{1i}	the selectivity coefficient
n	the number of electrons passing around the external circuit
R	the ideal gas constant
T	Kelvin temperature
z_1	the charge of the primary ion
z_i	the charge of an interfering ion

33 wt% PVC, 66 wt% plasticizer, 1 wt% ionophore, and a trace amount of membrane additives [1–10]. However, an excessive amount of plasticizer and ionophores in the polymer causes them to exude and/or leach out from the matrix while in use. Consequently, the sensor lifetime is reduced [6,7] and the exuded plasticizer and ionophores often lead to an unstable response during both short term and long term monitoring [8–10]. Techniques have been studied to overcome these problems related to leaching and adhesion of the ion sensor membranes. More recently, several procedures for grafting of various membrane components were used to prevent leaching [11–20], and the reduced use or elimination of the plasticizer from the membrane has also been attempted through the use of conventional polymers for ion-selective membranes (e.g., polysiloxane and polyurethane) [21–27].

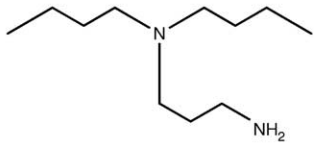
The objectives of this study are the preparation of Cr(VI) selective ionophore-immobilized membranes and the development of a stable ISE for the monitoring of Cr(VI) in wastewater. It is known that Cr(VI) forms complexes with specific ionophores in aqueous solutions, and several previous studies have reported that Cr(VI) forms complexes with ionophores comprised of tertiary amines or quaternary amines (e.g., trioctyl amine or Aliquat336). Therefore, it was considered that specific types of tertiary amine-containing monomers can be used as Cr(VI) selective ionophores depending on their structural property. In this study, *N*,*N*,*N*,*N*-tetrakis(3-aminopropyl)-1,4-butanediamine (DABAm4), *N*,*N*′,*N*″-trihexyldiethylenetriamine (ThDETA), and 3-(dibutylamino) propylamine (DPA) were selected as potential ionophores and were immobilized on PVC films. As the structures are illustrated in Fig. 1, these molecules may have a potential to form octahedral complex with Cr(VI). To immobilize these compounds onto the matrix, ultraviolet (UV)-induced graft polymerization was employed. Prior to introduction of the ionophore, glycidyl methacrylate (GMA) monomers were grafted on the PVC matrix and then the ionophores were covalently immobilized to the PVC matrix by reacting the epoxide of grafted GMA



N,N,N′,N′-tetrakis(3-aminopropyl)-1,4-butanediamine (DABAm4)



N,N′,N″-trihexyldiethylenetriamine (ThDETA)



3-(dibutylamino)propylamine (DPA)

Fig. 1. Molecular structures of the ionophores applied in this study.

with the primary/secondary amine of the ionophores. These ionophore-immobilized membranes were then evaluated according to their stability and selectivity for Cr(VI) using a potentiometric ISE.

2. Experimental

2.1. Reagents

For membrane preparation, poly(vinyl chloride), benzophenone (BP), glycidyl methacrylate, DABAm4, ThDETA, DPA, *o*-nitrophenyloctyl ether (NPOE), and tetrahydrofuran (THF), purchased from Aldrich chemicals (Milwaukee, WI), were used without further purification. $K_2Cr_2O_7$, for standard solutions of Cr(VI), and KCl, KNO_3, KNO_2, KI, KSCN, K_2SO_4, and K_2CO_3, for interference ions, were also purchased from Aldrich chemicals (Milwaukee, WI). All aqueous solutions were prepared with Milli-Q deionized water.

2.2. Membrane preparation

The ionophore-immobilized membranes were prepared by modifying the sequential photo-induced living graft polymerization suggested by Ma et al. [28] according to the following

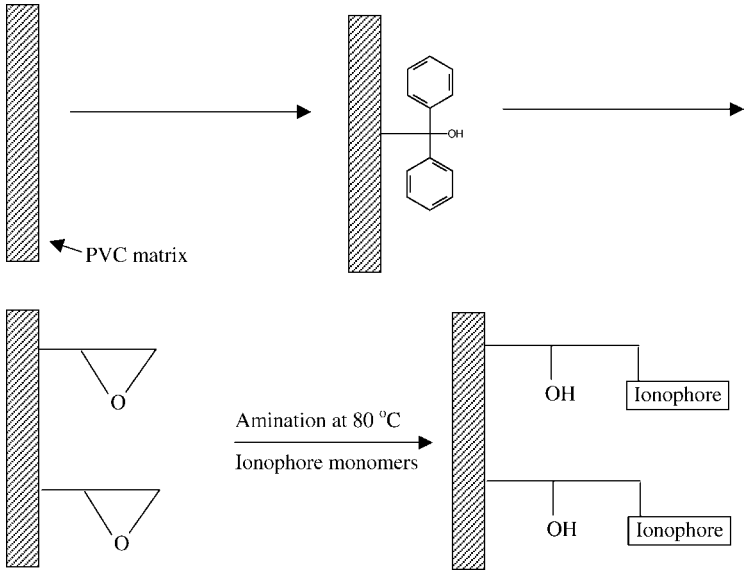


Fig. 2. Schematic procedure for membrane synthesis.

steps. The procedure for the preparation of the ionophore-immobilized membranes is described schematically in Fig. 2. Firstly, non-porous poly(vinyl chloride) thin films of about 0.03–0.05 mm thickness were prepared as a substrate in the THF solution. BP (5 wt% in methanol) was used as a photo initiator. Three grams of the initiator solution was poured onto the PVC films within a petri-dish (10 cm). After evaporation of the methanol, the film was placed in a quartz reaction vessel (20 cm × 15 cm × 4 cm) and nitrogen gas was purged throughout the vessel to reduce undesirable side reactions. Then the film was irradiated with UV light, using a mercury lamp (400 W, with a wavelength range of 110–400 nm) for 3 min to form radicals. Thirty weight percent GMA in methanol was used as an intermediate to covalently introduce ionophores into the PVC matrix since the epoxide of GMA can react with the primary and/or secondary amines of the ionophores. A total of 3.0–3.5 g of the GMA methanol solution were added onto the films and this was then irradiated with UV light for 8 min. The GMA-grafted films were then washed thoroughly in an ultrasonic bath consisting of methanol/acetone/water to remove homo-polymers and then dried in an oven at 60 °C for 1 day.

A 50 wt% DABAm4 aqueous solution and pure ThDETA and DPA, due to their hydrophobic nature, were used to introduce the ionophore to the GMA-grafted films. After the GMA-grafted films were immersed in each flask with the appropriate amount of the prepared solutions, they were reacted with the ionophores in a water bath for 3 days at 80 °C. The resulting films contained various concentrations of NPOE to form channels that allow Cr(VI) to permeate the membrane easily. The prepared membranes were cut into 5 mm × 5 mm pieces and applied in Cr(VI) ISE studies. The membranes prepared in this study were analyzed by FT-IR–ATR (JASCO, FT/IR 460 plus, Japan) to verify that the grafting was completed. Also morphological observation of the membranes was performed using a scanning electron microscopy (JEM-2010, JEOL, Japan) after the sample was mounted on a stub and coated with gold using an ion coater.

2.3. Measurement of the electromotive forces

The ionophore-immobilized membranes were placed in an electrode body to measure the electromotive forces of Cr(VI). A double junction electrode (ORION, 90-02, USA) filled with a 3.3 M KCl solution was used as the reference electrode. A Phillips electrode body (IS-561, Glasblaserie Moller, Zurich) was used as the working electrode to determine the Cr(VI) concentration in the test solutions. The effective area of the portable ISE membrane was 0.04 cm^2. The total volume of the inner filling solution was 1 ml with the concentrations of $K_2Cr_2O_7$ and KCl being 1.0×10^{-4} M each. The electromotive forces were measured by a computer based data acquisition system with a multi-meter (KOSENTECH, KST101A, Korea) and a detection time of 5 min for each sample. Solutions of KCl, KNO_3, KNO_2, KI, KSCN, K_2SO_4, and K_2CO_3 were employed to examine the effects of interfering ions. The selectivity coefficients of interferences for Cr(VI) were determined by the fixed interference method (FIM) recommended by IUPAC with concentrations of interfering ions of 1.0×10^{-3} M each. The detection limits of Cr(VI) in the presence of interferences were also estimated by FIM. Long-term responses of the ISE, with the optimized DABAm4-immobilized membrane, were examined to evaluate the membrane stability.

2.4. Cr(VI) selectivity

Bois et al. [44] reported that Cr(VI) could be adsorbed with amine functionalized silicas by an electrostatic interaction between the chromate anion and the hydrated amino-site.

Therefore, Cr(VI) may form strong complexes with amine-structured ionophores. The ionophore-immobilized membranes should be evaluated with respect to their high selectivity for the Cr(VI) ion against other co-ions (interfering ions). In this regard, an extraction method was employed to determine the distribution coefficients, k_d, of the Cr(VI) and interfering species. The extraction experiments were carried out under the following conditions. An optimized membrane was cut into 5 cm × 5 cm pieces (about 1.0×10^{-4} mol of the ionophores per piece) and immersed in 200 ml of an aqueous solution containing 1.0×10^{-3} M of Cr(VI) and each interfering ion. The resulting solutions were stirred at room temperature for 1 day, and then samples were taken to determine the remaining concentrations of the Cr(VI) and interfering ions using a UV–vis spectrophotometer (UV mini 1240, Shimadzu, Japan) at a wavelength of 540 nm and ion chromatography (DIONEX, DX-500, USA), respectively.

3. Results and discussion

3.1. Immobilization of ionophore

Fig. 3 shows the characteristic peak of FT-IR–ATR in each reaction step of the immobilization procedure—PVC, GMA-grafted PVC, and ionophore (DABAm4, ThDETA, and DPA)-immobilized PVC, respectively. In the GMA-grafted PVC, the absorption band assigned to carboxyl functional groups is seen at 1700 cm^{-1}, while that assigned to three-ring member ether (epoxy function) is observed at 910 cm^{-1}, indicating that GMA monomers are grafted onto the PVC matrix. In the DABAm4-immobilized PVC and the ThDETA-immobilized PVC, the absorption band assigned to the tertiary amine can be seen at 1359 cm^{-1}. Also, the absorption band assigned to hydroxyl function is observed in the range of 3200–3700 cm^{-1}, while the 910 cm^{-1} (epoxy function) band disappeared, implying that DABAm4 and ThDETA were both immobilized on the GMA-grafted PVC through amination to the epoxy ring. Such reactions resulted in the formation of a secondary hydroxyl group and the simultaneous disappearance of the epoxy ring. On the other hand, in the DPA-immobilized PVC, the absorption band at 910 cm^{-1} (epoxy function) was still apparent while the absorption band at 3200–3700 cm^{-1} (hydroxyl function) was weak, although the absorption band for the tertiary amine was observed, indicating that the degree of amination with DPA was lower than those with DABAm4 and ThDETA. Fig. 4 presents the degree of immobilization of the ionophores as a function of the time of amination. The results show that, for all the ionophores, the amount immobilized did not increase after 2 days of amination. The maximum degrees of immobilization of the ionophores were attained at 17 wt% DABAm4, 29 wt% ThDETA, and 6 wt% DPA, with respect to the PVC matrixes, respectively. It is believed that ionophore molecules were immobilized mainly on the membrane surface and partially in the membrane according to the result of FT-IR–ATR spectra and the weight-ratio of ionophore versus PVC matrix. It was expected that immobilization degrees exhibit the order of DABAm4 > ThDETA > DPA because, in term of functionality (number of primary or secondary amine), DABAm4 is 4, ThDETA is 2, and DPA is 1, respectively. However, the result showed a decreasing order of ThDETA > DABAm4 > DPA because the ionophores were aminated in different concentration; concentration of DABAm4 was 50 wt% in water whereas each concentration of ThDETA and DPA was 100 wt% (generally, in most reaction a degree of reaction is known to increase with increasing concentration). The result agreed well with that of FT-IR–ATR.

In this study, the sensitivity of Cr(VI) complexed with ionophores was evaluated analytically using a potentiometric method, although it can be estimated using chemical instruments—such as differential scanning calorimetry

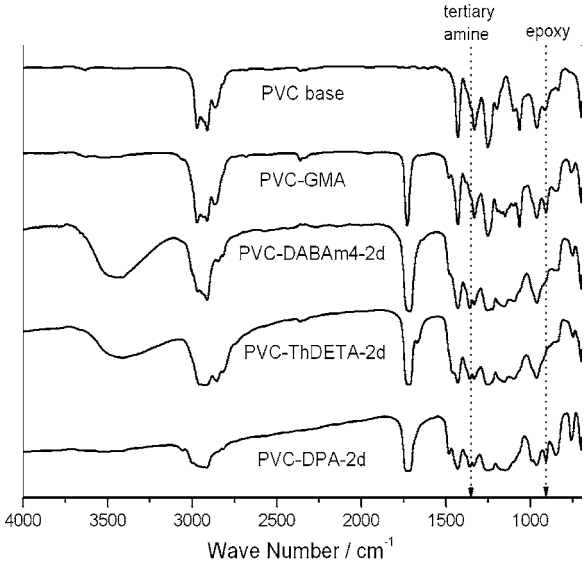


Fig. 3. FT-IR spectra of the ionophore-immobilized membranes (amination time: 2 days).

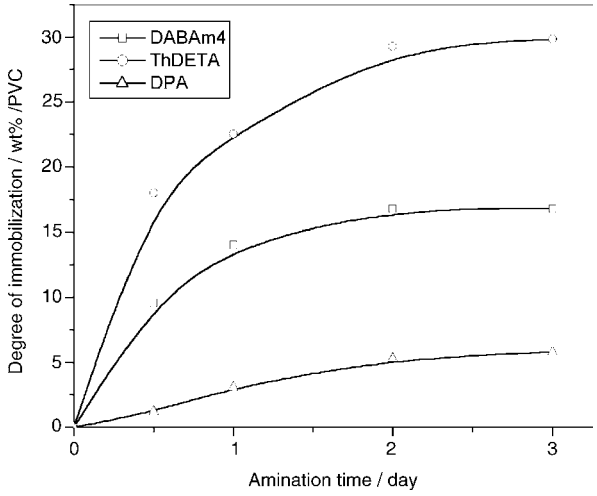


Fig. 4. Degree of immobilization as a function of amination time. The optimized grafting ratio of GMA to PVC was 30.4%.

(DSC) and nuclear magnetic resonance (NMR). Potentiometric ISEs have advantages in terms of their simplicity in controlling the sensitivity and the rapid determination. The potentiometric signals of the ISE membrane with ionophore (or carrier) for specific ions are qualitatively observed by changes in the capacity of the double layers formed within the boundary layer of the sample solution. Thus, a potentiometric ISE was employed to examine the sensitivity and selectivity of the ionophore-immobilized membranes prepared for Cr(VI) ions in this study. A modified Nicolski–Eisenman equation [29] was used to experimentally determine the Nernstian slopes, as shown in the following equation:

$$E = E_0 + \frac{RT}{nF} \ln \left(a_1 + \sum_{i=2}^{q} K_{1i}^{z_1/z_1} a_1^{1-z_i/z_1} a_i \right) \quad (1)$$

The fraction of chromate species in a solution depends on the pH according to equilibrium relations. In the pH range of 3.5–5.6, $HCrO_4^-$ and the orange–red dichromate ion CrO_4^{2-} are in equilibrium [30]. In this study, the test solutions were prepared at pH 3.5–6.0, where the predominant chromate species was the monovalent anion, $HCrO_4^-$ [31].

Fig. 5 shows the typical response sensitivity of the Cr(VI) ISE membranes prepared with various times of amination with the ionophores used. To neglect the effect of the plasticizer, a composition of 1.0 ml NPOE/g PVC for all the tested membranes was employed in the experiments. As shown in Fig. 5(a and b), stable responses from the DABAm4 and ThDETA membranes after being treated for 2 or more days were attained for various concentrations of Cr(VI) and the potential drift was no greater than ±2 mV during the experiments. The ISEs gave reasonably linear responses with a 1 s detection time for a wide range of concentrations (i.e., 2.16×10^{-6} to 0.1 M, with a detection limit of 0.225 ppm for DABAm4, and 7.97×10^{-6} to 0.1 M, with a detection limit of 0.829 ppm for ThDETA). On the other hand, the responses of the membranes treated with DABAm4 and ThDETA for less than 2 days were not acceptable due to their unstable sensitivity and unreasonable slope (theoretical response slope = −59.2 mV per decade) in the concentration range investigated in this study. Furthermore, tests done with the DPA-immobilized membranes revealed that the responses were very unstable and that the Nernstian slopes were not determined for the Cr(VI) ion sensitivity (see Fig. 5(c)). Therefore, the DPA-immobilized membrane was not feasible for Cr(VI) determination by ISE. The results of these tests show that appropriate ionophores should be immobilized in the PVC matrixes to ensure stable and sensitive responses.

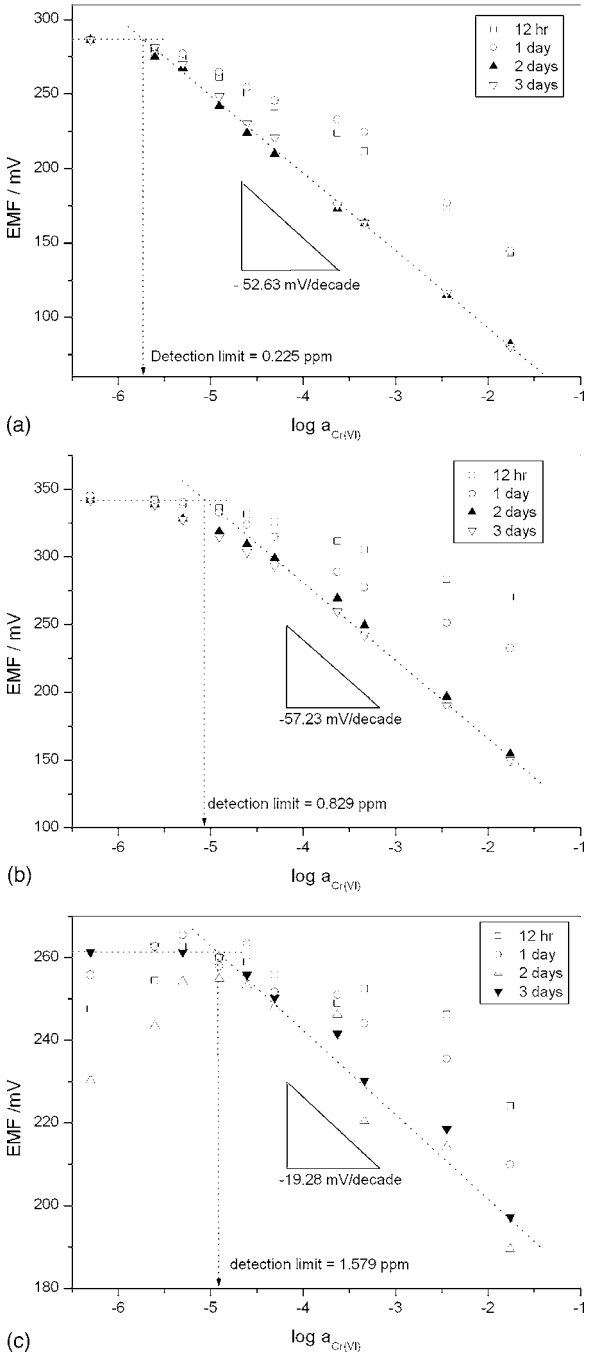


Fig. 5. Emf as a function of the Cr(VI) ion concentration for the ionophore-immobilized membranes entrapped with 1.0 ml NPOE/g PVC for various amination times: (a) DABAm4; (b) ThDETA; (c) DPA.

3.2. Effect of NPOE

The best way to prevent the leaching of membrane components into the solution is no use of a plasticizer in the membrane. However, in this study, an appropriate amount of plasticizer should be contained since the ionophore-immobilized membranes prepared without plasticizer are too dense to form channels in the membrane through which Cr(VI) can diffuse. A plasticizer plays an important role in the ionophore-immobilized membrane as it forms channels for selective ions, providing mobility to the ionophores bearing the ions within the membranes. NPOE was used as a plasticizer in this study due to its high electric permeability and hydrophobicity. The effects of NPOE content on the potentiometric responses of the membranes containing DABAm4 and ThDETA were also investigated and the results are presented

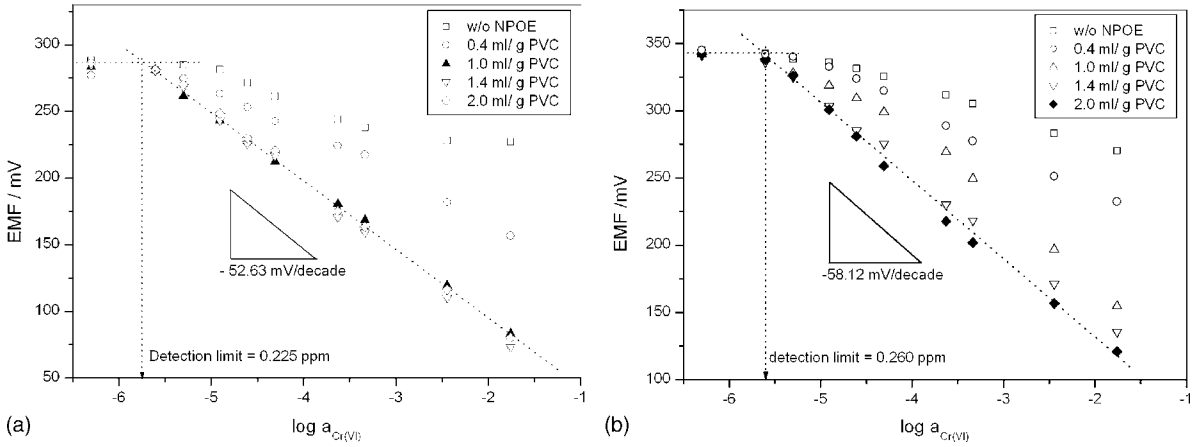


Fig. 6. emf as a function of the Cr(VI) ion concentration and the NPOE concentration for the ionophore-immobilized membranes that underwent amination for 2 days: (a) DABAm4 and (b)ThDETA; w/o NPOE; 1.0 ml NPOE/g PVC.

in Fig. 6. Changes in the emf values were observed for solutions tested under the same experimental conditions but with various amounts of NPOE, i.e., from 0 to 2.0 ml/g PVC. As shown in Fig. 6, in the cases where the NPOE concentrations were less than 1.0 ml/g PVC, the potentiometric responses were not only unstable but also insensitive to the Cr(VI) concentrations, clearly indicating that transfer of the Cr(VI) ions through the membrane was difficult without a reasonable number of channels, although the ions were selectively bound by the ionophore ligands. On the contrary, when 1.0 ml/g PVC or more was used, the potentiometric responses were stable and sensitive. These results were further investigated by observing the membrane morphologies with scanning electron microscopy (SEM), as presented in Fig. 7. The DABAm4-immobilized membrane without NPOE exhibited a physically tight structure, as shown in Fig. 7(a), while the membrane with NPOE (1.0 ml/g PVC) showed a physically loose and swollen structure that includes channels through which Cr(VI) ions can diffuse (see Fig. 7(b)). The SEM results are in agreement with the potentiometric response.

Meanwhile, the DABAm4-immobilized membranes plasticized with over 1.0 ml NPOE/g PVC gave similar responses (Fig. 6(a)). It implies that the response slope of a membrane with over 1.0 ml NPOE/g PVC should be almost same as that of the membrane with 1.0 ml NPOE/g PVC although the former has a physically looser and more swollen structure than the later has. In other words, NPOE concentration over 1.0 ml/g PVC in the membrane did not improve the channels further. The Nernstian slope was determined as −52.63 mV with the detection limit of 0.225 ppm in the membrane containing 1.0 ml NPOE/g PVC. On the other hand, ThDETA-immobilized membranes should contain 2.0 ml NPOE/g PVC to attain the response comparable with the optimized DABAm4-immobilized membranes (i.e., the slope was −58.12 mV with the detection limit of 0.260 ppm). The result shows that an amount of NPOE in the ThDETA-immobilized membranes required more than that in the DABAm4-immobilized membranes in order to optimize the ISE performance. Of the ionophore-immobilized membranes prepared in this study, the DABAm4-immobilized membrane with 1.0 ml NPOE/g PVC was found to be the most suitable ISE membrane for the determination of Cr(VI). In addition, the ratio of NPOE to PVC was reduced remarkably as compared with the previous PVC based ISEs [1–5] and was similar to the results investigated recently in methacrylate and epoxyacrylate based ISE systems [32–42].

3.3. Distribution coefficient

A hydrophobic solute has a distribution coefficient of greater than unity with a high mobility in the oil phase, while a hydrophilic solute has a distribution coefficient of far less than unity. A hydrophilic solute is not easily extracted into the hydrophobic phase (i.e., the membrane entrapped with NPOE) without an assistant carrier. The distribution coefficients of the Cr(VI) and interfering ions were evaluated using the following equation:

$$\text{distribution coefficient, } k_d = \frac{\text{concentration of the ion extracted into the membrane}}{\text{equilibrium concentration of the ion remaining in the solution}} \quad (2)$$

The DABAm4-immobilized membrane and the ThDETA-immobilized membrane, both with 1.0 ml NPOE/g PVC, were used to estimate distribution coefficients of the Cr(VI) and interfering ions. The results are listed in Table 1. All the tested interfering ions had k_d values far below unity for the DABAm4-immobilized membrane. In spite of the hydrophilic properties of Cr(VI), its distribution coefficient was relatively higher than that of the interfering ions. The selectivity of Cr(VI) against the other ions was in the order of $SO_4^{2-} > Cl^- > NO_2^- > NO_3^- > HCO_3^- > I^- > SCN^-$ for the DABAm4-immobilized membrane. For the ThDETA-immobilized membrane, the k_d values for all the interfering

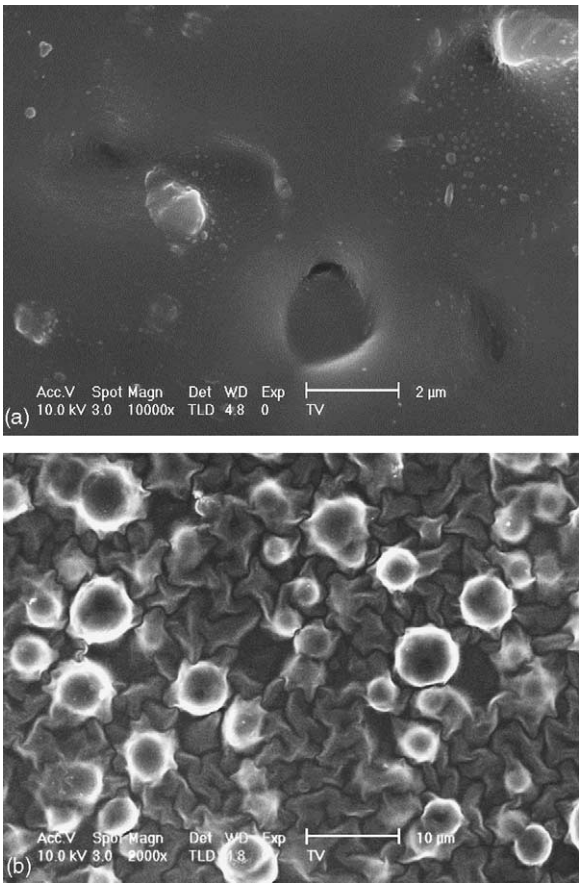


Fig. 7. Scanning electron microscope pictures of the surfaces of the DABAm4-immobilized membranes (a) without NPOE and (b) with 1.0 ml NPOE/g PVC.

ions were also below unity. Nevertheless, the selectivity of Cr(VI) against these ions was much lower than that of the DABAm4-immobilized membrane. In this case, I^- and SCN were more selective than Cr(VI). Although the ISEs with ThDETA-immobilized membranes containing NPOE gave sensitive responses to Cr(VI) (Fig. 6(b)), the membranes are not feasible for use in the determination of Cr(VI) ions in the presence of interfering ions due to their low selectivity. The above results imply that the formation of the octahedral Cr(VI) complex with the six-member-amine structured ionophore was easier than with a three-member-amine structured ionophore. Therefore, the DABAm4-immobilized membrane, entrapped with 1.0 ml NPOE/g PVC, was used as the ISE membrane in the following experiments.

Table 1
Distribution coefficients of the Cr(VI) and interfering ions for the membranes containing DABAm4 and ThDETA according to the extraction method

Ionic matter	DABAm4		ThDETA	
	k_d	*Selectivity	k_d	*Selectivity
Cr(VI)	0.77	1	0.55	1
Cl^-	2.32×10^{-3}	3.01×10^{-3}	0.24	0.44
NO_2^-	3.31×10^{-2}	4.29×10^{-2}	2.73×10^{-2}	4.96×10^{-2}
NO_3^-	5.40×10^{-2}	7.01×10^{-2}	4.47×10^{-2}	8.13×10^{-2}
SO_4^{2-}	6.54×10^{-4}	8.49×10^{-4}	3.64×10^{-3}	6.62×10^{-3}
HCO_3^-	7.56×10^{-2}	9.81×10^{-2}	0.13	0.24
I^-	0.15	0.19	0.66	1.20
SCN^-	0.57	0.74	0.58	1.05

Remark: *Selectivity = distribution coefficient of the interference/distribution coefficient of Cr(VI).

3.4. Effect of interfering ions

It is also important to evaluate effects of interfering ions on the selectivity of Cr(VI) when using the ISE with the optimized DABAm4-immobilized membrane. The selectivity of an electrode membrane is determined not only by the ion mobility or the strength of association between the ions, but also by such factors as the ionic strength and the ion concentration ratio. The selectivity coefficient, K_{1i}, was calculated using the optimized DABAm4-immobilized membrane by the fixed interference method [43] with the following equation:

$$K_{1i} = \frac{a_1}{a_i^{z_1/z_i}} \quad (3)$$

Fig. 8 shows the potentiometric response of the test solution containing the interfering ions using FIM. The results indicate that Cr(VI) was stably determined, in the presence of interfering ions, when using the ISE with the optimized DABAm4-immobilized membrane, at a cost of the slightly decreased detection limit.

Table 2 summarizes the selectivity coefficients and detection limits of Cr(VI) in the presence of the interfering ions for the optimized DABAm4-immobilized membrane. The tendencies seen in the selectivity were similar to those of the extraction method and reasonably comparable with the literature values [3–5]. The K_{1i} values show that the DABAm4-immobilized membrane was more selective to Cr(VI) against the interfering ions. From the above results, it is believed that the six-member amine-structured DABAm4 formed stronger

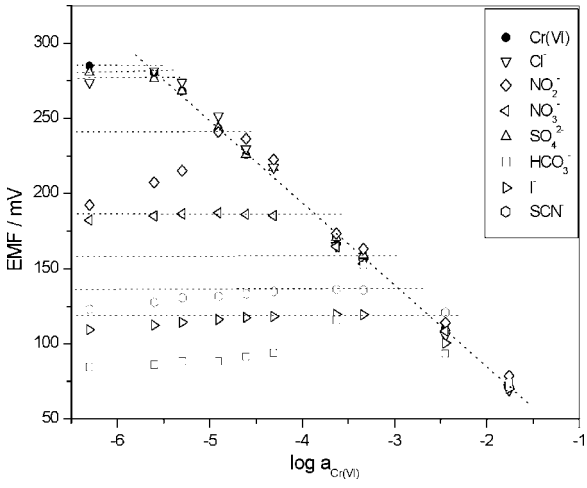


Fig. 8. Effect of interfering ions on the ISE according to the FIM method when using the optimized DABAm4-immobilized membrane with various concentration of Cr(VI) ions. Interfering ions were added at a concentration of 1E−3 M each and the concentration of the inner filling solution was 1E−4 M each of $K_2Cr_2O_7$ and KCl.

Table 2
Selectivity coefficients and detection limits of the Cr(VI) ion in the presence of the interfering ions for the optimized DABAm4-immobilized membrane

Interference	K_{1i}^{FIM}	$\log K_{1i}^{FIM}$	Detection limit of Cr(VI)/M (ppm)
Cl^-	5.62×10^{-3}	−2.25	3.00×10^{-6} (0.313)
NO_2^-	2.82×10^{-2}	−1.55	1.41×10^{-5} (1.469)
NO_3^-	0.27	−0.57	1.44×10^{-4} (15.03)
SO_4^{2-}	1.82×10^{-4}	−3.74	2.49×10^{-6} (0.259)
HCO_3^-	0.389	−0.41	4.68×10^{-4} (48.64)
I^-	4.69	0.67	2.40×10^{-3} (249.5)
SCN^-	2.40	0.38	1.15×10^{-3} (119.4)

Table 3
Comparison of ISE performances for Cr(VI) between this study and previous studies

	Ionophore	Membrane type	Nernstian slope (mV per decade)	Potential drift (mV)	Detection range (ppm)	Detection limit (ppm)	Long-term stability
This study	DABAm4	**IIM	−52.6	±2	0.1–5000	0.225	Over 6 months
Rudoi et al. [3]	Diphenyl carbazide	***SLM	+18.0	±2	1–5000	About 1	Maximum 2 months
Choi and Moon [4]	Trioctyl phosphate (TOPO)	***SLM	+19.6	±2	0.1–100	0.1	1 month
Choi and Moon [5]	Tricaprylmethyl ammonium chloride (Aliquat336)	***SLM	−53.7	±2	1–5000	1.05	2–3 months

Remarks: **IIM and ***SLM refer to ionophore-immobilized membrane and supported liquid membrane, respectively.

complexes with Cr(VI) than the interferences since Cr(VI) forms stably complexes with the hydrated amino structured ionophores.

3.5. Response stability

The purpose of immobilizing the ionophores in a polymer matrix is to examine whether the immobilized ionophores could function in an ion-selective membrane without being leached. Fig. 9 shows the results of a long-term test on the response stability. Within the time interval studied, the Nernstian slopes were found to be relatively stable at −54.61 mV, within ±2.45 mV potential drifts, and the detection limits were 0.239 ppm (2.29E−6 M) with a 5.8% deviation for 4 months. The optimized ISE allows reliable analysis for a long period if the electrodes are calibrated periodically. These results demonstrate that the membrane determined Cr(VI) selectively and rapidly with stable potential values during the lifetime, and that the detection limit was further improved compared to previous studies [3–5], as presented in Table 3.

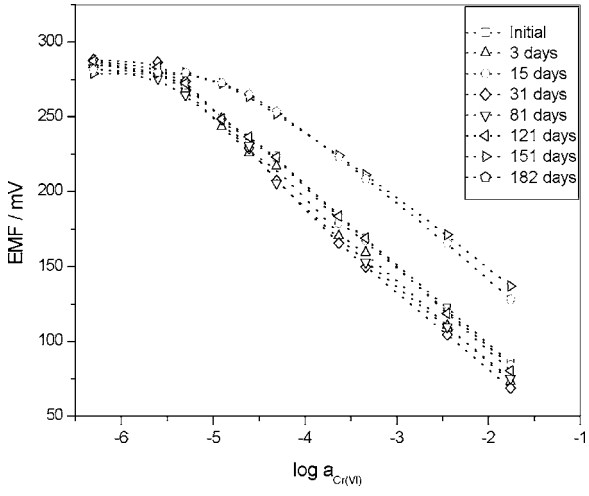


Fig. 9. Response stability of the ISE to Cr(VI) ions over a long-term experiment using the optimized DABAm4-immobilized membrane.

However, the membrane sensitivity for Cr(VI) decreased slightly due to the leaching out of membrane additives during the 4 month extended performance. The Nernstian slope was determined to be −51.02 mV and the detection limit slowly decreased to 0.328 ppm after 6 months. This loss in sensitivity is due to the leaching out of membrane ingredients into the test solution [44]. Fig. 10 shows the comparison of FT-IR–ATR spectra between the virgin DABAm4-immobilized membrane and the membrane used for 6 months.

To observe the tertiary amine functional groups within the membrane, NPOE within the membrane was removed by rinsing the membrane with methanol and then washed repeatedly with Milli-Q deionized water. The absorption band assigned to tertiary amine was clearly apparent at 1359 cm^{-1}, indicating that DABAm4 did not leach out from the membrane during the test. From the results of the FT-IR–ATR spectra, it was confirmed that the decrease in the sensitivity of the membrane during a long-term ISE performance was caused by the exudation of NPOE rather than the leaching-out of DABAm4. It is thought that the loss

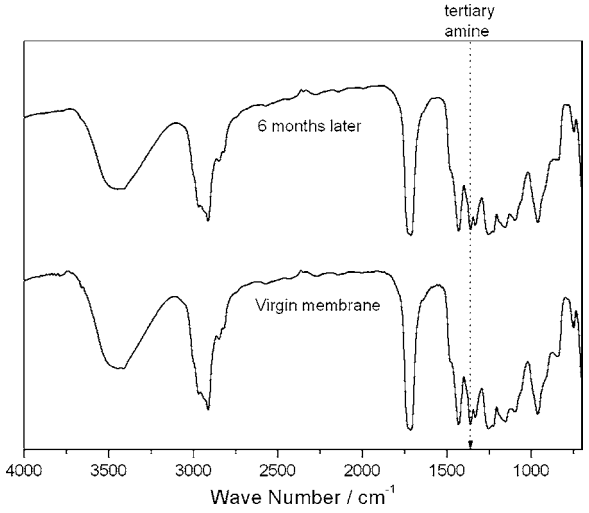


Fig. 10. FT-IR spectra comparison between the virgin membrane and the membrane employed for 6 months in Fig. 9.

of NPOE alone from the membrane led to the loss of the performance.

4. Conclusions

Novel ionophore-immobilized membranes for determination of Cr(VI) in wastewater were prepared by sequential UV-induced graft polymerization and amination technique. DABAm4 was found to be a new Cr(VI) selective ionophore. One millilitres NPOE/ g PVC in the DABAm4 immobilized membrane was employed for forming Cr(VI) diffusible channels. Cr(VI) ISE performances using the DABAm4 immobilized membrane were improved rather than the previous studies with respect to the detection range and limit of Cr(VI) and stability. Cr(VI) was sensitively detective in the presence of the various interfering ions using the ISE with the DABAm4 immobilized membrane in aqueous solutions. From the result of FT-IR spectra, it was confirmed that there was no change in the immobilized tertiary amine group, DABAm4, on the membrane even though Cr(VI) sensitivity decreased slightly due to exudation of NPOE for a long-term experiment. Consequently, it is suggested that the ISE with the DABAm4 immobilized membrane is not only adaptable for stable determination of Cr(VI) but also feasible and reproducible for monitoring of Cr(VI) in wastewater. Nevertheless, there is still great room for improvement in the present ISE membrane. Because no use of plasticizer in the DABAm4 immobilized membrane will advance in response stability and sensitivity for long-term monitoring using the Cr(VI) ISE, further works for improvement of the membrane should hereafter be examined.

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