

Trace-Level Potentiometric Detection in the Presence of a High **Electrolyte Background**

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Supporting Information

ABSTRACT: Polymeric membrane ion-selective electrodes (ISEs) have become attractive tools for trace-level environmental and biological measurements. However, applications of such ISEs are often limited to measurements with low levels of electrolyte background. This paper describes an asymmetric membrane rotating ISE configuration for trace-level potentiometric detection with a high-interfering background. The membrane electrode is condi- NaL* tioned in a solution of interfering ions (e.g., Na⁺) so that no primary ions exist in the ISE membrane, thus avoiding the ion-exchange effect induced by high levels of interfering ones in the sample. When the electrode is in contact with the primary ions, the interfering ions



in the membrane surface can be partially displaced by the primary ions due to the favorable ion-ligand interaction with the ionophore in the membrane, thus causing a steady-state potential response. By using the asymmetric membrane with an ion exchanger loaded on the membrane surface, the diffusion of the primary ions from the organic boundary layer into the bulk of the membrane can be effectively blocked; on the other hand, rotation of the membrane electrode dramatically reduces the diffusion layer thickness of the aqueous phase and significantly promotes the mass transfer of the primary ions to the sample-membrane interface. The induced accumulation of the primary ions in the membrane boundary layer largely enhances the nonequilibrium potential response. By using copper as a model, the new concept offers a subnanomolar detection limit for potentiometric measurements of heavy metals with a high electrolyte background of 0.5 M NaCl.

C ince the discovery of lowering the detection limit of ion-Selective electrodes (ISEs) in 1997,¹ spectacular progress in the development and application of potentiometric sensors has been made, and the new wave of ISEs has already arrived.²⁻⁴ The lower detection limit of polymeric membrane ISEs has been improved by a factor of up to 10^6 , while the discrimination of interfering ions has even improved by a factor up to $10^{10.5}$ Nowadays, ISEs have evolved to be a promising technique for trace-level environmental and biological measurements.⁶⁻⁹ However, it should be noted that most of the applications of polymeric membrane-based ISEs developed so far are limited to measurements with low levels of electrolyte background, typically for drinking water^{10,11} or well-controlled solutions.^{8,9} Very few polymeric membrane ISEs have been reported for potentiometric detection with a high-interfering background. The ISE with an optimal internal solution buffered for primary ions has been used for determination of low levels of calcium with an intracellular fluid background containing high concentrations of K⁺, Na⁺, and Mg²⁺.¹² To avoid super- or sub-Nernstian behavior, tedious optimization of the inner solution is required for each sample. By coupling the microliter potentiometric detection to an efficient online electrochemical accumulation step, solid-contact ion-selective microelectrodes

have been used for monitoring cadmium ions at low parts per billion levels in samples containing a 0.5 M NaCl background electrolyte.¹³ However, this approach needs more sophisticated instrumentation and longer measurement procedures.

Herein, we introduce a simple and effective methodology for direct trace-level potentiometric detection with a highinterfering background. We show that by using an asymmetric membrane rotating ISE configuration, the accumulation of primary ions in the boundary layer of the ISE membrane phase can largely enhance the nonequilibrium steady-state potential response, which offers a subnanomolar detection limit for measuring heavy metals in the presence of a high-background electrolyte.

EXPERIMENTAL SECTION

Reagents. High molecular weight poly(vinyl chloride) (PVC), 2-nitrophenyl octyl ether (o-NPOE), sodium tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), the lipophilic salt tetradodecylammonium tetrakis(4-chlorophenyl)-

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borate (ETH 500), and the Cu²⁺ ionophore *N,N,N',N'*tetradodecyl-3,6-dioxaoctane-dithioamide (ETH 1062) were purchased from Fluka AG (Buchs, Switzerland). The H⁺ ionophore 4-(octadecylamino)azobenzene (ETH 5315) was synthesized as described previously.¹⁴ NaCl was Suprapure from Sigma-Aldrich. Tetrahydrofuran (THF) was freshly distilled prior to use. All other reagents were analytical grade and used without any further purification. Aqueous solutions were prepared with freshly deionized water (18.2 M Ω cm specific resistance) obtained with a Pall Cascada laboratory water system. A stock solution of 0.01 M Cu²⁺ was prepared by dissolving CuCl₂ in deionized water and then diluted to various concentrations of working solutions with 0.5 M NaCl.

Membranes and ISEs. The conventional Cu²⁺-ISE membranes contained (in wt %) ETH 1062 (1), NaTFPB (1), o-NPOE (65), and PVC (33), while the hard membranes contained (in wt %) ETH 1062 (1), NaTFPB (1), o-NPOE (28), and PVC (70). The asymmetric membranes were prepared by evenly spreading 5 μ L of a NaTFPB solution (0.734 mg/mL in THF) on the surface (8 mm diameter) of the membrane matrix containing (in wt %) ETH 1062 (1), ETH 5315 (0.5), ETH 500 (1), o-NPOE (27.5), and PVC (70) and letting the active layer dry for 1 h. The components of each membrane (totaling 180 mg) were dissolved in THF (2.5 mL) and poured into a glass ring (i.d. 36 mm) fixed on a glass plate. Overnight evaporation of the solvent yielded transparent membranes of ~100 μ m thickness. For each ISE, an 8 mm diameter disk was punched from the membranes and glued to a plasticized PVC tubing with a THF/PVC slurry. Solutions of NaCl (0.5 and 0.01 M) were used as the internal filling solutions for the detection of copper in saline solutions and evaluation of the selectivity coefficients, respectively. All the electrodes were conditioned in a solution identical to the inner filling solution for 1 day.

EMF Measurements. A rotating silver disk electrode (ATA-1B, Jiangsu Jiangfen Electroanalytical Instrument Company, Ltd.) with a diameter of 3 mm was used as an internal reference electrode. The silver disk electrode was chloridized with a solution of 1 M HCl containing 0.1 M FeCl₃. The plasticized PVC tubing with the asymmetric ISE membrane glued at the distal end was filled with the internal filling solution of 0.5 M NaCl and then screwed onto the silver disk electrode. The external reference electrode employed was a doublejunction saturated calomel electrode (SCE) with 0.1 M LiOAc as a bridge electrolyte. All measurements were performed with a rotating (at 3000 rpm) or nonrotating mode configuration (with a stir bar operating at 200 rpm for sample convection¹⁵). Electromotive force (EMF) values were measured at 20-21 °C using a PXSJ-216 Leici pH meter (Shanghai, China) in the galvanic cell: SCE/0.1 M LiOAc/sample solution/ISE membrane/inner filling solution/AgCl/Ag.

Selectivity coefficients were determined by a separate solution method.¹⁶ The EMF values were corrected for the liquid-junction potentials with the Henderson equation. The ion activity coefficients were calculated according to the Debye–Hükel equation.

RESULTS AND DISCUSSION

It has been established that the detection limits of polymeric membrane ISEs can largely be influenced by the leaching of primary ions from the sensing membrane into the sample solution.^{17–21} Such ion release is a consequence of zero-current ion fluxes generated by concentration gradients within the

membrane caused by coextraction of primary ions with their counterions from the inner electrolyte solution into the inner surface layer of the membrane and/or by the ion exchange of primary ions in the outer surface layer of the membrane with interfering ions from the sample. With ion-buffered inner solutions or by using solid-contact ISEs, the coextraction effect can be effectively eliminated.²² However, interfering ions from the sample solution may partially replace the primary ions in the outer boundary layer of the membrane phase and induce substantial fluxes of primary ions from the membrane into the sample. It has been shown that the exchange of a very small fraction of primary ions by interfering ions could significantly hamper the attainable detection limits of ISEs.²⁰ Therefore, it is essential to avoid the ion-exchange processes of primary ions with interfering ions for sensitive potentiometric measurements with a high electrolyte background.

In this work, copper was tested as a model heavy metal for trace-level potentiometric measurements in a saline background of 0.5 M NaCl, which is typical for seawater. Unlike the conventional polymeric membrane electrodes which are conditioned with primary ions before measurements, the proposed electrode is conditioned with the saline background of 0.5 M NaCl so that the highly discriminated ions (i.e., Na⁺) are initially present in the interfacial layer of the membrane phase. In this case, no ion exchange of primary ions in the membrane phase by interfering ions in the sample solution would occur. Rather, when the electrode is in contact with the sample solution containing Cu²⁺ in 0.5 M NaCl, the primary ions can rapidly replace the discriminated ions due to the favorable ion-ligand interaction with the ionophore (i.e., ETH 1062) in the membrane. Figure 1 shows the time-dependent potential response traces of four discriminated-ion-conditioned Cu²⁺-selective electrodes. As can be seen, a strong super-Nernstian response occurs at low levels of the primary ions for the ISE of type A, which has a conventional membrane composition with a PVC content of 33 wt %. Similar observations were reported by Hulanicki for the EMF responses of chloride-conditioned anion-exchanger-based membrane electrodes toward low levels of lipophilic anions such as perchlorate and periodate.²³ The electrode behavior was fully explained via a steady-state model.²⁴ Such a super-Nernstian nonequilibrium mechanism was later successfully applied to sensitive detection of polyions in saline solution (e.g., 0.12 M NaCl), for which a steady-state potential response is observed when the flux of polyion from the sample solution equals the flux in the polymeric membrane.^{25,26} Interestingly, the nonequilibrium steady-state sensing mode can also be used for potentiometric measurements of smaller ions (e.g., Cu²⁺) with a high electrolyte background. Since the EMF response of the proposed discriminated-ion-conditioned electrode is highly dependent on the accumulation of primary ions in the interfacial layer of the membrane phase, the detection sensitivity can largely be improved by accelerating ion fluxes in the aqueous Nernst layer and/or suppressing ion fluxes from the phase boundary into the bulk of the membrane. Indeed, potential responses to lower levels of Cu^{2+} were observed by using a rotating disk electrode which reduces the stagnant aqueous diffusion layer (type B).¹⁵ In addition, using a hard membrane (with 70 wt % PVC) could further increase the potential response due to the decrease in the diffusion rate of the primary ions in the membrane (type C). 25 However, it should be noted that the diffusion coefficients of heavy metals (e.g., Cu²⁺) are much larger than those of polyions, which



Time / s

Figure 1. Potentiometric responses to copper in 0.5 M NaCl by using different discriminated-ion-conditioned ISE membranes: type A, conventional membrane with 33 wt % PVC (nonrotating mode); type B, conventional membrane with 33 wt % PVC (rotating at 3000 rpm); type C, hard membrane with 70 wt % PVC (rotating at 3000 rpm); type D, asymmetric membrane with a thin layer of ion exchanger on the membrane matrix of 70 wt % PVC (rotating at 3000 rpm).

would induce faster diffusion of the primary ions within the membrane phase so that less primary ions could be accumulated in the surface boundary layer of the membrane.

To effectively block the diffusion of the primary ions in the membrane, an asymmetric polymeric membrane electrode was constructed. In this method, the lipophilic ion-exchanger (i.e., NaTFPB) is loaded on the surface layer of the polymeric membrane rather than being incorporated into the whole ISE membrane matrix as for conventional ISEs. The diffusion of primary ions away from the boundary layer into the bulk of the membrane can be prevented, owing to the absence of ionic sites in the membrane bulk.^{21,25} In this case, the primary ions will readily accumulate in the interfacial layer of the membrane rather than diffuse further into the membrane bulk. Thus, a lower detection limit can be achieved. The asymmetric membrane was formed by evenly spreading the ion-exchanger solution in THF (5 μ L) onto the PVC membrane surface (8 mm diameter). The formation of the asymmetric membrane was examined visually by a microscope. Since the lipophilic ion exchanger is colorless, Rhodamine 6G was employed as an

independent probe to indicate the formation of two layers. The active layer of $\sim 7 \,\mu m$ thickness was observed on the surface of the ISE membrane of $\sim 100 \ \mu m$ thickness, which confirms the formation of the asymmetric sensing membrane. Since no ion exchanger was added in the membrane bulk, a lipophilic electrolyte (i.e., ETH 500) was incorporated into the membrane to decrease the resistance of the polymeric membrane.²⁷ The potential response associated with the asymmetric membrane is shown in Figure 1 (type D). Clearly, the ISE based on the asymmetric membrane shows a significantly improved performance. For measurements of Cu^{2+} at 10^{-7} M, the EMF change obtained by the asymmetric membrane electrode (type D) is approximately 130 mV while those by the electrodes with homogeneous membranes (types C and B) are 7 and 2 mV, respectively. These results indicate that the transmembrane ion fluxes of primary ions are largely suppressed by using the asymmetric membrane.

Interestingly, such suppression can be further confirmed by the sample stirring effect. As described above, a steady-state response can be obtained when the flux of the primary ion from the sample solution equals the flux through the polymeric membrane. A sudden stop of sample stirring or electrode rotation would significantly reduce the ion flux in the aqueous phase but not affect the ion flux in the membrane, thus dramatically decreasing the concentration of the primary ion accumulated in the membrane surface. Indeed, as shown in Figure 1, for the membrane with ion exchanger present inside the membrane (type C), the potential response decreases rapidly when rotation of the membrane electrode is stopped. However, this sample stirring effect is much less pronounced for the asymmetric membrane electrode (type D) because of the effective inhibition of the ion flux from the phase boundary into the bulk of the membrane. It should be noted that the ion fluxes in the membrane cannot be completely blocked because inherent impurities in the PVC matrix would work as ion exchangers.

Experiments were further conducted for optimization of experimental parameters. The effect of the amount of the ion exchanger loaded on the membrane surface layer was investigated. The concentrations of the ion exchanger in THF were varied from 0.2 to 3.0 mg/mL. As shown in Figure S1 of the Supporting Information, the EMF response increases with increasing the concentration of the ion exchanger up to 0.7 mg/ mL, which is attributed to the increase in ionic sites on the surface of the membrane for effective ion exchange at the sample-membrane interface; however, further increase in the concentration of the ion exchanger loaded on the surface of the asymmetric membrane could cause smaller potential responses. Therefore, the NaTFPB concentration of 0.7 mg/mL with a maximum response was chosen for the proposed electrode. Since the nonequilibrium steady-state response of the asymmetric membrane electrode can be greatly improved by using the rotating electrode configuration,^{15,28} the effect of the rotation speed on the sensitivity of the electrode was examined. As shown in Figure S2 of the Supporting Information, the potential response increases rapidly with rotation speed up to 3000 rpm and then tends to increase gradually. Experiments also showed that the noise levels became much bigger at rotation speeds above 3000 rpm. Therefore, 3000 rpm was chosen as the optimal rotation speed.

A typical calibration curve of the asymmetric membrane rotating electrode for measuring Cu^{2+} at concentrations ranging from 1.0 to 200 nM with a background of 0.5 M NaCl is shown

in Figure 2. The potential response to the concentration of Cu²⁺ is linear in the range of 1.0–100 nM (E = 0.59 + 1.29C, γ



Figure 2. Time-dependent EMF response traces of the asymmetric membrane rotating electrode for measuring Cu^{2+} in the presence of a 0.5 M NaCl background. The upper left inset shows the corresponding calibration curve. The other conditions are as given in Figure 1 (type D).

= 0.999, with *E* given in mV and *C* in nM). The time to achieve 95% of the full-scale steady-state response is 7-10 min. The detection limit was calculated to be 0.35 nM, which gives a potential signal equal to the blank signal plus three times the standard deviation of the blank measurement (n = 11). It should be noted that for measurements at concentrations higher than 10^{-6} M, the primary ions (i.e., Cu²⁺) can fully displace the discriminated ions (i.e., Na⁺) from the interfacial layer of the membrane. In this case, the sample-membrane phase boundary is at equilibrium, and thus the Nernstain electrode responses can be observed. The selectivity coefficients of the asymmetric membrane for Cu2+ over interfering ions were determined by using Bakker's method to eliminate the influence of the inherent sensitivity limit on the ISE response toward discriminated ions.¹⁶ The results are summarized in Table 1. As can be seen, most of the potentiometric selectivity coefficients of the asymmetric membrane-based ISE are comparable to those of the conventional ISE with the homogeneous membrane. According to the amount of NaTFPB coated on the surface of the PVC membrane and the thickness of the active layer observed, the molar ratio of

Table 1. Potentiometric Selectivity Coefficients, $log_{Cu,J}^{pot}$, of the Proposed Asymmetric Membrane ISE Compared with Those Obtained with the Conventional Membrane ISE

	log ^{pot} ^a	
ion J	asymmetric membrane ^b	conventional membrane ^c
H^+	-4.1 ± 0.2	-8.0 ± 0.5
Na^+	-11.2 ± 0.1	-10.8 ± 0.1
K^+	-8.6 ± 0.4	-8.9 ± 0.2
Mg ²⁺	-13.4 ± 0.4	-13.9 ± 0.5
Ca ²⁺	-11.7 ± 0.3	-11.4 ± 0.1
Pb ²⁺	-1.1 ± 0.5	-0.5 ± 0.2
Zn^{2+}	-5.5 ± 0.2	-4.9 ± 0.4

^{*a*}Mean value obtained from three corresponding pairs of concentrations of Cu²⁺ and the respective interfering cation in the Nernstian response range \pm SD. ^{*b*}The asymmetric membrane consisted of a membrane matrix containing (in wt %) ETH 1062 (1), ETH 5315 (0.5), ETH 500 (1), *o*-NPOE (27.5), and PVC (70) and an active surface layer of NaTFPB. ^{*c*}The conventional membrane contained (in wt %) ETH 1062 (1), NaTFPB (1), *o*-NPOE (65), and PVC (33).

NaTFPB/ionophore for the asymmetric membrane was estimated to be 0.3 (see the Supporting Information), which is close to the ratio of 0.5 as for the conventional polymeric membrane. The difference in the selectivity coefficients for H⁺ ions is due to the incorporation of a neutral proton-selective ionophore in the proposed asymmetric membrane (see below). Negligible potential responses to copper using a membrane without the ionophore (Figure S3 of the Supporting Information, curve A) and to interfering ions using the asymmetric membrane (Figure S3 of the Supporting Information, curves B to D) in the NaCl background prove that the recorded responses shown in Figure 2 are indeed related to the ionophore and not only to the cation-exchange process facilitated by TFPB⁻ on the membrane surface. The high sensitivity and excellent selectivity of the proposed asymmetric-membrane rotating electrode offer promising potential for trace-level potentiometric detection in the presence of a high electrolyte background, especially for seawater and biological fluid samples.

Since the asymmetric membrane electrode shows high selectivity over discriminated ions, it is rather difficult to strip Cu^{2+} from the asymmetric membrane by reconditioning the electrode with the electrolyte background before the next measurement. To improve the sensor's reversibility, the pH cross-sensitive electrode was designed for which a neutral proton-selective ionophore (ETH 5315) is incorporated in the membrane together with the copper-selective ionophore (ETH 1062).²⁹ The membrane restoration was accomplished by stripping Cu²⁺ out of the membrane with an acid solution. The renewal principle is analogous to that of the heparin sensor described earlier.³⁰ The logarithmic Nikolskii coefficient of the asymmetric membrane for H^+ was measured as $-4.1 (\pm 0.2)$. Experiments show that the H⁺ ions can be quickly exchanged into the interfacial layer of the polymeric membrane at pHs lower than 4. By using an acid solution of pH 3, the feasibility for the stripping of Cu^{2+} from the asymmetric membrane was tested. The results are shown in Figure 3. As illustrated, the potential responses are fully reversible with a good reproducibility of 0.3 mV standard deviation (10 nM, n = 6).

The diffusion of the ion exchanger from the membrane surface into the bulk of the plasticized membrane could gradually change the composition of the active interfacial layer. Therefore, the lifetime of the proposed asymmetric ISE membrane was investigated by measuring the responses to copper ions in 0.5 M NaCl with the same membrane on



Figure 3. Recycle potential responses of the asymmetric membrane Cu^{2+} ISE to 10 nM Cu^{2+} and to the 0.5 M NaCl background. Each measurement was followed by a 20 min stripping with 10^{-3} M HNO₃ and by 1 h of reconditioning in a pH 8.0 phoshate buffer containing 0.5 M NaCl. The other conditions are as given in Figure 1 (type D).

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different days. The results are shown in Figure S4 of the Supporting Information. It can be seen that no significant change in the sensitivity of the membrane electrode is observed within two weeks. Such stability of the asymmetric membrane might be attributed to the high PVC content in the membrane matrix which prolongs the penetration of the ion exchanger from the surface layer into the membrane bulk.³¹

CONCLUSIONS

A novel strategy of constructing asymmetric membrane rotating disk ISEs has been demonstrated. The response mechanism of the proposed ISE sensing mode is based on the nonequilibrium steady-state diffusion process of primary ions at the sample– membrane interface. The concept offers a subnanomolar detection limit for measuring heavy metals in 0.5 M NaCl. Since many ionophores with excellent selectivities have been extensively exploited, the present methodology may pave a new way to develop polymeric membrane ion-selective electrodes for trace-level potentiometric detection of various ionic species in the presence of a high electrolyte background, especially for marine and biological environments.

ASSOCIATED CONTENT

S Supporting Information

Experimental details and additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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