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Sensing of Poly(styrenesulfonate)s by Polymeric Membrane Electrodes Based on Liquid Anion-Exchangers

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The potentiometric responses of ion-selective electrodes (ISEs) based on various liquid anion-exchangers for poly(styrenesulfonate)s (PSSs) were examined. The liquid anion-exchangers included lipophilic monoammonium, monophosphonium, diphosphonium, and triphosphonium salts. The molecular weights of PSSs, which had narrow molecular-weight distributions ($M_w/M_n < 1.2$), were varied from 1.8×10^3 (PSS-1.8K) to 3.5×10^4 (PSS-35K). For PSS-1.8K, ISEs based on diphosphonium salts, polymethylenebis(trioctylphosphonium) dibromides **1—3**, exhibited good responses, the response slope and linear response range being −20 to −21 mV/decade and 5.0×10^{-5}—5.0×10^{-3} equiv dm^{-3}, respectively. As the molecular weight of PSS was increased, the linear response range became smaller, while the response slope was almost constant. Finally, PSS-35K gave almost no response. On the other hand, a wide molecular-weight distribution PSS ($M_w/M_n = 3.6$) provided a good response, although it had a high average molecular weight ($M_w = 1.6\times10^4$). The selectivity coefficients for PSS over various anions of ISEs, based on diphosphonium and monophosphonium salts, were assessed.

So far, a large number of studies have been carried out concerning polymeric membrane-based ion-selective electrodes (ISEs).[1—3] However, only a few studies involving ISEs for polyion species have been performed. We briefly reported on a polymeric membrane electrode which responds to poly(styrenesulfonate)s (PSSs) by using a lipophilic diphosphonium salt, hexamethylenebis(trioctylphosphonium) dibromide, as the sensing material.[4] A sensor for a polyanionic saccharide, heparin, in which tridodecylmethylammonium chloride is used as the sensing material, has been developed.[5,6] In the heparin sensor, the response is ascribed to a nonequilibrium change in the phase boundary potential.[7] Hattori et al. reported sensing of PSSs by using tetradecyldimethylbenzylammonium chloride (Zephiramine).[8]

A coal-water mixture (CWM) comprising powdery coal, water, and a small amount of dispersant is an attractive utilization of coal and one of the most promising alternatives for heavy oil. For such a dispersant, PSSs are mainly used, and the distribution of PSS between the surface of coal and the aqueous phase of CWM is very important for the fluidity and stability of CWM. We investigated such a distribution of PSS in CWM by using the PSS-responsive ISE.[9]

However, the feature and response mechanism of the ISE has not yet been clarified. In the present study, we investigated in detail the sensing of PSSs by ISEs based on various liquid anion-exchangers; a remarkable feature of the ISEs is described. The liquid anion-exchangers include lipophilic monoammonium, monophosphonium, diphosphonium, and triphosphonium salts. The effects of the molecular weight of PSSs and the molecular-weight distribution upon the potentiometric response were examined. In addition, the potentiometric selectivity for PSS of the ISEs over various anions was assessed. The response mechanism is discussed in comparison with other polyion-responsive ISEs.

Experimental

Chemicals. Poly(vinyl chloride) (PVC) with an average polymerization degree of 1100 and dioctyl phthalate were purchased from Wako Pure Chemicals. The molecular-weight standard sodium poly(styrenesulfonate)s, which have narrow molecular weight distributions ($M_w/M_n < 1.2$; M_w: weight-average molecular weight; M_n: number-average molecular weight), were obtained from Pressure Chemical Co. (Pittsburgh, PA). These polymers, having molecular weights of 1.8×10^3, 4.0×10^3, 5.4×10^3, 8.0×10^3, 1.8×10^4, 3.5×10^4, and 8.8×10^4, are abbreviated as PSS-1.8K, PSS-4K, PSS-5.4K, PSS-8K, PSS-18K, PSS-35K, and PSS-88K, respectively. A sodium poly(styrenesulfonate) ($M_w = 1.6\times10^4$; PSS-CWM), which has a very wide molecular-weight distribution ($M_w/M_n = 3.6$) and are utilized for the additive of coal-water mixture (CWM),[9—12] was donated by Lion Corporation. Deionized water was prepared by passing distilled water through an Organo G-10 cartridge.

Lipophilic diphosphonium salts (polymethylenebis(trioctylphosphonium) dibromides **1—3**), a monophosphonium salt (buyltrioctylphosphonium bromide **4**), and a triphosphonium salt **6** are known compounds.[13,14] Methyltrioctylammonium chloride (Capriquat, **5**) was purchased from Dojindo Laboratories. The structures of these liquid anion-exchangers are indicated in Fig. 1.

Solvent Extraction. An aqueous solution (5.0 mL) of a sodium poly(styrenesulfonate) (1.0×10^{-3} equiv dm^{-3}) and sodium bromide (3.0—40 mM; 1 M = 1 mol dm^{-3}) were shaken with a 1,2-dichloroethane solution (5.0 mL) of the anion-exchanger (1.0×10^{-3} equiv dm^{-3}; 0.50 mM for **2** or 1.0 mM for **4**) for 30 min in a 50 mL stoppered centrifuge tube at 24—25 °C with a Yamato Model SA-31 shaker. After phase separation, the concentration of PSS in the aqueous phase was measured by a Hitachi Model U-2000 UV-

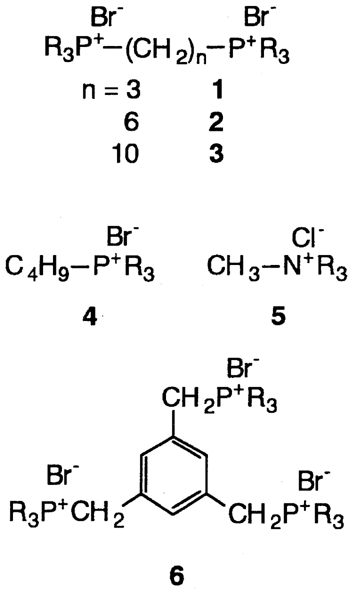

Fig. 1. Structures of liquid anion-exchangers ($R = C_8H_{17}$).

vis spectrophotometer (260 nm). The amount of PSS extracted into the organic phase was taken as the difference between the amount initially added and that determined after equilibrium in the aqueous phase. In some runs, the material balance on the PSS distribution between the aqueous and organic phases was confirmed by back-extraction experiments.

Preparation of PVC Membrane for ISE. PVC (0.40 g), dioctyl phthalate (1.0 g), and the anion-exchanger (0.20 g) were dissolved in 10 mL of tetrahydrofuran (THF). The THF solution was poured onto a flat Petri dish and THF was allowed to slowly evaporate at room temperature. A piece of the PVC membrane was attached to a PVC tube, and the resulting tube was fixed on a Denki Kagaku Keiki (DKK) number 7900 electrode body. A portion of an aqueous solution of KCl (10 mM) was added as an internal solution for the ISE. The ISE was conditioned by soaking in an aqueous solution of the PSS (5.0×10^{-4} equiv dm^{-3}) to be measured for two days before use.

ISE Measurements. Potentiometric measurements with the membrane electrode were carried out at 24—25 °C with a voltage meter (DKK PHL-40 pH meter), a double-junction Ag–AgCl reference electrode (DKK number 4083), and a magnetic stirrer to agitate the sample solution. The electrode cell was Ag–AgCl/10 mM KCl/PVC membrane/sample solution/10 mM KCl/3.0 M KCl/Ag–AgCl. Sodium sulfate (20 mM) was added to the sample solution as a supporting electrolyte.

The selectivity coefficients for PSS-CWM relative to other anions (X^-) ($K^{\mathrm{Pot}}_{\mathrm{PSS,X}}$) of **2**-ISE and **4**-ISE were determined by the Matched potential method.[15] The background concentration of PSS-CWM was 5.0×10^{-4} equiv dm^{-3}. The $K^{\mathrm{Pot}}_{\mathrm{PSS,X}}$ values were calculated from the concentration of the interfering ion which induced the same change in the ISE potential when the concentration of PSS-CWM was increased to 3.0×10^{-3} equiv dm^{-3}.

Results and Discussion

Solvent Extraction of PSSs. The solvent extraction of PSSs from aqueous solutions into 1,2-dichloroethane by a diphosphonium anion-exchanger **2** or a monophosphonium anion-exchanger **4** was performed. The concentration of **4** initially added to the organic phase was twice that of **2**. Therefore, the cationic charge concentration in the organic phase was the same for both the dicationic and monocationic anion-exchangers. Table 1 gives the values of % Extraction for the solvent extraction of PSSs, which include PSS-5.4K, PSS-8K, PSS-35K, and PSS-88K. As the concentration of NaBr in the aqueous phase increased, the extractability of PSS decreased. This result suggests that PSSs are extracted into the organic phase by an anion-exchange reaction with bromide anions. As the molecular weight of PSS increased, the extractability of PSS was reduced. Thus, it is anticipated that PSSs having higher molecular weights are more hydrophilic.

It has been reported that when liquid anion-exchangers possessing two cationic centers in the molecule, such as **2**, the extractability of the dianionic species (naphthalenedisulfonates, phthalates, aspartate derivatives, anionic metal complexes, etc.) are much greater than those of the corresponding monocationic anion-exchangers, such as **4** and **5**.[13,14,16—19] As can be seen in Table 1, also for the extraction of polyanionic species PSSs, **2**, which is a dicationic anion-exchanger, was much superior to a monocationic anion-exchanger **4**. It appears that dicationic anion-exchangers have higher affinities to PSSs than do monocationic anion-exchangers.

Potentiometric Responses of ISEs Based on Various Anion-Exchangers for PSS-1.8K. Liquid anion-exchangers **1**—**6** were incorporated into solvent polymeric membranes in which PVC was the polymer and dioctyl phthalate was the membrane solvent. The potentiometric responses for PSS-1.8K were measured using ISEs prepared from the membranes (Fig. 2). When monocationic anion-exchangers, such as **4** and **5**, were used, potentiometric response slopes of -16 mV/decade and linear response ranges of 3×10^{-4}—5×10^{-3} equiv dm^{-3} were obtained. There was no significant difference between the response for **4**, a phosphonium salt, and that for **5**, an ammonium salt.

For dicationic anion-exchangers **1**—**3**, potentiometric response slopes of -20 to -21 mV/decade and linear response ranges of 5×10^{-5}—5×10^{-3} equiv dm^{-3} were obtained. The better responses found when dicationic anion-exchangers **1**—**3** were used may be rationalized by considering the better affinities of the dicationic anion-exchangers to PSSs compared to those with monocationic anion-exchangers. There was no significant change when the length of

Table 1. Extraction of PSSs by Liquid Anion-Exchangers[a)]

Compd[b)]	NaBr	% Extraction			
	mM	PSS-5.4K	PSS-8K	PSS-35K	PSS-88K
2	10	96	90	83	72
2	20	85	71	56	35
2	40	56	54	30	28
4	3	52	50	42	35
4	20	c)	c)	c)	c)

a) Extraction conditions are seen in the text. b) Structures are shown in Fig. 1. c) % Extraction < 5%.

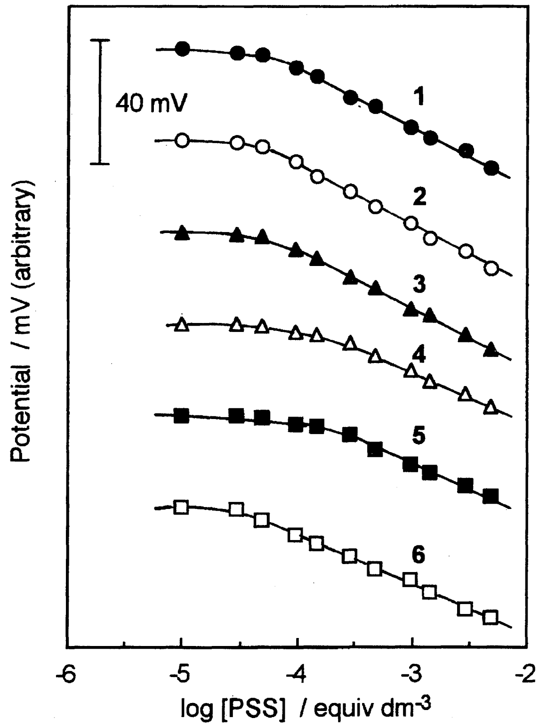

Fig. 2. Potentiometric responses for PSS-1.8K by ISEs based on **1**—**6**.

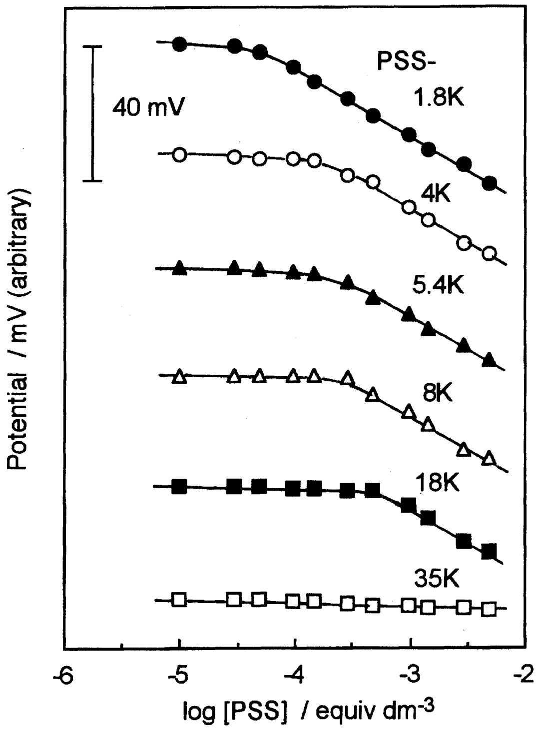

Fig. 3. Potentiometric responses for PSSs of various molecular weights by an ISE based on **2**.

methylene chain between two cationic centers was changed from three to ten. When *o*-nitrophenyl octyl ether (NPOE) was used as a membrane solvent instead of dioctyl phthalate, a similar result was obtained. A tricationic anion-exchanger **6** provided a large linear response range (3×10^{-5}—5×10^{-3} equiv dm^{-3}), although the response slope was rather low (−16 mV/decade).

Response of ISE for PSSs of Various Molecular Weight. The potentiometric responses for molecular-weight standard PSSs having various molecular weights were measured using an ISE based on **2** (Fig. 3). The variation in the molecular weight includes 1.8×10^3, 4.0×10^3, 5.4×10^3, 8.0×10^3, 1.8×10^4, and 3.5×10^4. A polymeric membrane which contained an anion-exchanger was conditioned in a solution of the PSS to be measured. As the molecular weight of PSS was increased, the linear response range became smaller, while the response slope was almost constant. Finally, PSS-35K, which has a molecular weight of 3.5×10^4, provided almost no response. When a polymeric membrane which had been conditioned in a solution of PSS-1.8K was utilized, the ISE exhibited almost no response to PSS-35K, as was observed for a membrane conditioned in a solution of PSS-35K.

The extractability of PSS-35K by liquid anion-exchangers was smaller than that of lower molecular-weight PSSs, such as PSS-5.4K (Table 1). However, the extraction of PSS-35K still considerably occurred. Thus, the poor responses found when higher molecular-weight PSSs were measured cannot be ascribed to the lower extractability of these PSSs. It is known that lower molecular-weight solutes more favorably diffuse through membranes in ultrafiltration; however, higher molecular-weight solutes undergo more friction in the membranes.[20,21] Therefore, the dependence of the ISE response upon the molecular weight of PSS may be rationalized by considering the diffusion of PSS in the polymeric PVC matrix membrane. It is proposed that PSSs having lower molecular weights favorably diffuse through a membrane compared with PSSs having higher molecular weights. Thus, the response range for higher molecular-weight PSSs would be smaller.

Table 2 gives the response slopes and the lower limits for a linear response when the potentiometric responses for PSSs of various molecular weights are measured using ISEs based on **1**—**4** and **6**. As can be seen in Table 2, dicationic anion-exchangers **1**—**3**, which have trimethylene, hexamethylene, and decamethylene units between two phosphonium cationic centers, provided about the same responses for PSSs. Compared with **1**—**3**, monocationic anion-exchanger **4** and tricationic anion-exchanger **6** gave lower slopes for the responses of all PSSs.

Response of ISE for PSS-CWM. Compared with molecular-weight standard PSSs, which have narrow molecular-weight distributions ($M_w/M_n < 1.2$), PSS-CWM, which is practically utilized as an additive of coal-water mixture (CWM),[9—12] has a wide molecular weight distribution ($M_w/M_n=3.6$; $M_w=1.6\times10^4$). The potentiometric responses for PSS-CWM were measured using ISEs based on anion-exchangers **1**—**4** and **6** (Fig. 4). The response slopes and the lower limits for the linear response are also recorded in Table 2.

Although PSS-CWM has a quite high weight-average molecular weight ($M_w = 1.6\times10^4$), the linear-response limit for PSS-CWM was about ten-times lower than that for PSS-

Table 2. Potentiometric Response Slopes and Linear Response Limit for Sensing of PSSs

Compd[a)]	PSS-1.8K		PSS-5.4K		PSS-8K		PSS-18K		PSS-35K	PSS-CWM	
	Slope (mV/decade)	Limit[b)]	Slope (mV/decade)	Limit[b)]	Slope (mV/decade)	Limit[b)]	Slope (mV/decade)	Limit[b)]	Slope	Slope (mV/decade)	Limit[b)]
1	21	5	21	30	21	30	20	50	c)	24	5
2	20	5	20	30	20	30	20	50	c)	23	5
3	20	5	20	30	20	30	20	50	c)	23	5
4	16	30	16	30	16	30	8	100	c)	17	20
6	15	3	12	30	12	30	12	30	c)	12	1

a) Structures are shown in Fig. 1. b) Lower limit for linear response ($\times 10^5$ equiv dm^{-3}). c) Slope is nearly zero.

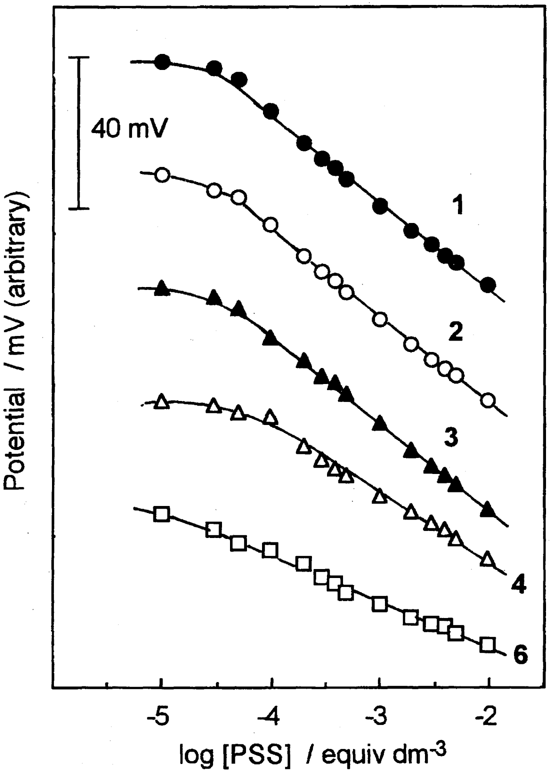

Fig. 4. Potentiometric responses for PSS-CWM by ISEs based on **1**—**4** and **6**.

18K, which has a similar molecular weight, when ISEs based on dicationic anion-exchangers **1**—**3** were used. The response behavior for PSS-CWM was similar to that for PSS-1.8K. It thus appears that the response of ISEs is dependent not only on the molecular weight of PSSs, but also on the molecular-weight distribution. Also, for PSS-CWM, dicationic anion-exchangers were superior to monocationic anion-exchangers in terms of the response slope and linear-response range.

ISEs based on **2** showed only a slight diminution of their initial response to PSS-CWM (slope and linear response range) after 100 days with a measurement every two or three days.

Selectivity Coefficients for PSS-CWM over Small Anions. The potentiometric selectivities for PSS-CWM over small anions, such as Cl^-, Br^-, NO_3^-, I^-, and benzoate, were determined by the Matched potential method[15] (Table 3). When an ISE based on **2**, which is a dicationic anion-exchanger, was used, the response to anions decreased in the following order: PSS−CWM > benzoate > I^- > NO_3^- > Br^- > Cl^-, which almost parallels the Hofmeister series.[22] Compared with **4**, which is a monocationic anion-exchanger, the $\log K^{Pot}_{PSS,X}$ values for **2** were more negative by 0.37—0.12 units. It appears that the ISE based on dicationic anion-exchangers is also superior to that of monocationic anion-exchangers in terms of the potentiometric selectivity.

Table 3. Selectivity Coefficients of ISEs Based on **2** and **4** for PSS-CWM over Various Anions

Anion (X)	$-\log K^{Pot}_{PSS,X}$ [a)]	
	2-ISE	**4**-ISE
$C_6H_5CO_2^-$	0.74	0.54
I^-	0.98	0.86
NO_3^-	1.26	1.01
Br^-	1.37	1.04
Cl^-	1.86	1.49

a) The selectivity coefficients were calculated by use of the equivalent of PSS-CWM.

Response of ISE for Mixtures of PSS-5.4K and PSS-35K. To probe the dependence of the potentiometric response upon the molecular weight of PSS and the molecular-weight distribution, mixtures of PSS-5.4K and PSS-35K in which the mixing ratio was varied from 1 : 1 to 1 : 16 were measured by an ISE based on **2**. As previously mentioned, PSS-5.4K provided a linear response with a slope of −20 mV/decade over a range of 3×10^{-4}—5×10^{-3} equiv dm^{-3}; however, PSS-35K gave almost no response (Fig. 3). As can be seen in Fig. 5, the mixtures in 1 : 1, 1 : 2, 1 : 4, 1 : 8, and 1 : 16 ratios exhibited responses with slopes of −20 mV/decade, −19 mV/decade, −18 mV/decade, −17 mV/decade, −14 mV/decade, respectively. The linear-response ranges for the 1 : 1, 1 : 2, and 1 : 4 mixtures were about the same as that for PSS-5.4K alone; however, the 1 : 8 and 1 : 16 mixtures gave somewhat narrow linear range (5×10^{-4}—5×10^{-3} equiv dm^{-3}). It is proposed that when even a small amount of low molecular-weight PSSs is present, the ISE becomes responsive to high-molecular weight PSSs, such as PSS-35K.

This fact may be explained as follows. When only PSS-35K is present in the solution, the diffusion in the polymeric membrane does not go well, because the high molecular weight PSS undergoes a large friction in the membrane.

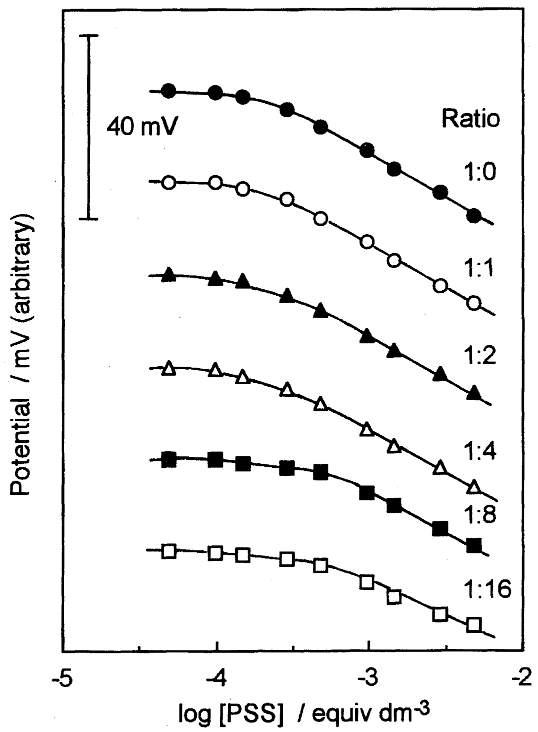

Fig. 5. Potentiometric responses for mixtures of PSS-5.4K and PSS-35K in which the mixing ratio was varied to include 1 : 0 (PSS-5.4K alone), 1 : 1, 1 : 2, 1 : 4, 1 : 8, and 1 : 16.

However, when a small amount of PSS-5.4K is added to the PSS-35K solution, the low molecular-weight PSS favorably diffuses in the membrane. It is proposed that each monomeric unit of whole PSSs which involve PSS-35K can interact with the cationic site on the membrane surface. Thus, the presence of a small amount of low molecular-weight PSSs may enable the surface interaction to be reflected to the ISE response. Therefore, even the 1 : 8 and 1 : 16 mixtures of PSS-5.4K and PSS-35K can produce good responses which are comparable to those for the low molecular weight PSSs. Since the molecular-weight distribution of PSS-CWM is quite wide, the PSS should contain low molecular-weight PSSs. This would be for the same reason that PSS-CWM, which has a wide molecular-weight distribution, gives a good response.

Comparison with Other Polyanion-Responsive Electrodes. For the heparin-responsive ISE, a steady-state kinetic process, in which a nonequilibrium change occurs in the phase boundary potential, has been proposed.[7] The main limitation of the ISE is that the response is not completely reversible. When the ISE is placed in a solution containing high levels of heparin, an additional rinsing step with a 1—2 M NaCl solution is required in order to obtain reproducible potential values.

However, for the present ISE, which responds to PSSs, the polymeric membranes are conditioned for two days in a solution of the PSS to be measured. It appears that the interface between the organic membrane phase and the aqueous sample solution phase is at equilibrium, as is observed for conventional ISEs responsive to small ions. Thus, the present ISE is as easy to handle as the conventional ISEs. It is anticipated that each or some aggregation of monomeric anion-units (styrenesulfonate anion units) in PSS works as an isolated ion at the interface, which gives an equilibrium potentiometric response (ca. −20 mV/decade) comparable to that for trivalent anions.

Hattori et al. reported on a flow-through PSS sensor in which Zephiramine is dissolved in the internal aqueous solution of the ISE, while the ISE membrane consists of only PVC and NPOE.[8] It appears that Zephiramine permeates through the membrane and interacts with PSSs at the interface between the membrane and the outer aqueous solution. The flow-through ISE exhibits almost a slope of −59 mV/decade comparable to that for monovalent anions. This would be explained by picture in which the potential observed is provided by the diffusion of Zephiramine in the membrane, so that the slope for monovalent ions is obtained and the ISE responds to even high molecular-weight PSSs. In present PSS-responsive ISE, since the liquid anion-exchangers in the membrane are more lipophilic than Zephiramine, the liquid-anion exchangers almost remain in the membrane. It appears that the potential observed is provided by the diffusion of PSSs.

Conclusions. The feature of PSS-responsive ISE were assessed. ISEs based on dicationic anion-exchangers, such as **1**—**3**, were superior to those of monocationic anion-exchangers in terms of response slope, linear response range, and selectivity for PSS. The response of the ISE was dependent on the molecular weight of PSS as well as the molecular-weight distribution. It was found that ISEs based on **1**—**3** provided stable and reproducible responses to polyanionic species, which have wide molecular-weight distributions, for a long time. Compared to other polyanion-responsive ISEs which require flow-through or additional rinsing processes so far reported, it should be an advantage for the present ISE that the ISE is as easy to handle as conventional ISEs.

References

1) M. D. Moody and J. D. R. Thomas, "Ion-Selective Electrodes in Analytical Chemistry," ed by H. Freiser, Plenum Press, New York (1978), Vol. 1, pp. 287—309.

2) M. E. Meyerhoff and W. N. Opdyeke, *Adv. Clin. Chem.*, **25**, 1 (1986).

3) Y. Umezawa, "Handbook of Ion-Selective Electrodes: Selectivity Coefficients," CRC Press, Boca Raton, FL (1990).

4) A. Ohki, K. Kawamoto, K. Naka, and S. Maeda, *Anal. Sci.*, **8**, 85 (1992).

5) S-C. Ma, V. C. Yang, and M. E. Meyerhoff, *Anal. Chem.*, **64**, 694 (1992).

6) S-C. Ma, V. C. Yang, B. Fu, and M. E. Meyerhoff, *Anal. Chem.*, **65**, 2078 (1993).

7) B. Fu, E. Bakker, J. H. Yun, V. C. Yang, and M. E. Meyerhoff, *Anal. Chem.*, **66**, 2250 (1994).

8) T. Hattori and M. Kato, *Anal. Sci.*, **11**, 285 (1995).

9) A. Ohki, M. Tsurugasaki, T. Nakajima, K. Naka, and S. Maeda, "Proc. 20th Int. Conf. on Coal Utilization and Fuel Systems," Clearwater, Florida, 1995, Abstr., p. 75.

10) T. Ogawa, M. Tanoura, and A. Hirai, *Bull. Chem. Soc. Jpn.*, **66**, 1343 (1993).

11) T. Ukigai, H. Sugawara, and N. Tobori, *Chem. Lett.*, **1995**,

371.

12) A. Ohki, S. Fukuda, K. Naka, and S. Maeda, *Sekiyu Gakkaishi*, **39**, 129 (1996).

13) A. Ohki, M. Yamura, S. Kumamoto, S. Ide, S. Maeda, and T. Takeshita, *Solvent Extr. Ion Exch.*, **7**, 57 (1989).

14) A. Ohki, S. Maeda, T. Takeshita, and M. Takagi, *Chem. Lett.*, **1987**, 1349.

15) V. P. I. Gadekpo and G. D. Christian, *Anal. Chim. Acta*, **164**, 279 (1984).

16) S. Ide, A. Ohki, and M. Takagi, *Anal. Sci.*, **1**, 349 (1985).

17) A. Ohki, M. Yamura, S. Kumamoto, S. Maeda, T. Takeshita, and M. Takagi, *Chem. Lett.*, **1989**, 95.

18) A. Ohki, M. Yamura, Y. Sumiyoshi, M. Takagi, and S. Maeda, *Anal. Sci.*, **6**, 291 (1990).

19) A. Ohki, H. Dohmitsu, and S. Maeda, *Bull. Chem. Soc. Jpn.*, **64**, 476 (1991).

20) S. Nakao and S. Kimura, *J. Chem. Eng. Jpn.*, **14**, 32 (1981).

21) S. Nakao and S. Kimura, *J. Chem. Eng. Jpn.*, **15**, 200 (1982).

22) Y. Shibata, S. Ozawa, N. Oki, and H. Miyagi, *Bunseki Kagaku*, **41**, 5 (1992).