

Sensing of Anionic Polymers by an Ion-Selective Electrode Based on Dionium Reagents

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Ion-selective electrodes (ISE) are widely used as an analytical tool for ionic species in aqueous media. However, to our knowledge, few studies have so far dealt with the determination of ionic polymers such as polystyrenesulfonate (PSS).

Although the application of anionic polymers, such as naphthalenesulfonate-formaldehyde condensate (NSF) and PSS, has been limited until quite recently, nowadays these polymers attract much attention as dispersants for coal water mixtures (CWM). CWM is the most promising alternative fuel for oil, so much research has been devoted to it.^{1,2} The behavior of dispersants in CWM has not yet been clarified, mainly because of the lack of appropriate determination methods for such compounds in CWM.

In a previous paper, we developed a new ISE selective to NSF by use of a lipophilic diphosphonium salt as a sensing material.³ The ISE method was effectively applied to the analysis of NSF behavior in CWM. In this study we investigate the determination of other anionic polymers including PSS and polydicyclopentadienesulfonate (PDCS) using the ISE method, demonstrating its general applicability.

Experimental

The synthesis of polymethylenebis(trioctylphosphonium) homologues (abbreviated as C_nBP, Fig. 1) was

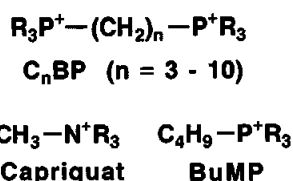


Fig. 1 Sensing materials (R=C₈H₁₇).

described elsewhere.⁴ The membrane of ISE was prepared by a usual method.⁵ A mixture of poly(vinyl chloride) (PVC) (0.4 g), dioctyl phthalate (1.0 g), and the sensing material (C_nBP·dibromide, 0.2 g) was dissolved in 10 ml of tetrahydrofuran (THF). The THF solution was poured onto a flat Petri dish and THF was allowed to evaporate slowly at room temperature. A piece of the PVC membrane was attached to the PVC tube of a liquid membrane electrode kit (Denki Kagaku Keiki (DKK) 7900) with THF. A portion of an aqueous solution containing 10 mM (1 M=1 mol dm⁻³) KCl was added as an internal solution of the ISE. The ISE was conditioned by soaking it in a 100 mg l⁻¹ solution of the anionic polymer to be measured for 2 d.

Potentiometric measurements with the ISE were carried out at 25 °C with an ion meter (DKK IOC-10) and a double junction Ag/AgCl reference electrode (DKK 4083) while agitating the sample solution with a magnetic stirrer (200 rpm). Sodium sulfate (20 mM) was added to the sample solution as a supporting electrolyte.

PSS (sodium salt, $\bar{M}_w=ca. 15000$) and PDCS (sodium salt, $\bar{M}_w=ca. 10000$) were donated by Lion Corporation and Japan Synthetic Rubber Co., Ltd., respectively. PSS for the standard of gel permeation chromatography (PSS-GPC, $\bar{M}_w=1800$) was purchased from Chemco Scientific Co., Ltd.

Results and Discussion

Figure 2 (a) shows a potential response of the ISE based on a dionium reagent, C₆BP, to PSS. The plot exhibits a good linearity (21.3 mV decade⁻¹) in a concentration range of 2 – 2000 mg l⁻¹. As seen in Fig. 2 (d and e), the C₆BP-ISE also showed good responses to PSS-GPC and PDCS.

It is very difficult to correctly determine the dispersant in highly loaded CWMs, because fine coal particles and

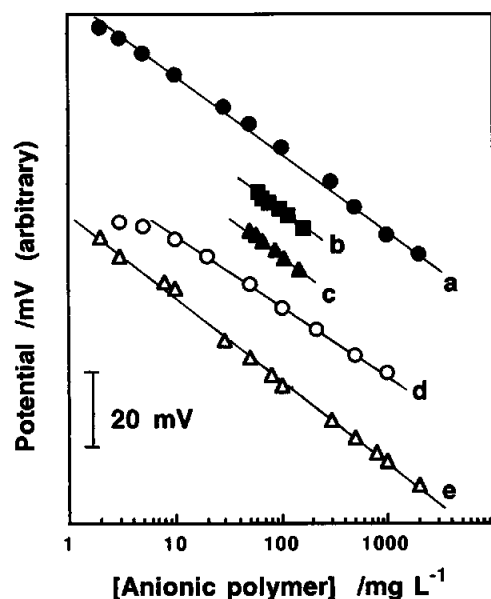


Fig. 2 Potential response of C_6BP -ISE to anionic polymers. a, PSS; b and c, PSS (calibration curves by the method of standard addition after shaking with powdery Workworth-coal and Datong-coal, respectively); d, PSS-GPC; e, PDCS.

various contaminants elutriating from the coal interfere with the determination. We therefore investigated the influence of the addition of powdery coal on the ISE determination. A solution of PSS (0.4 wt%; 10 ml) was shaken with 10 g of powdery coal (200 mesh) for 20 h, and its filtrate was analyzed by the ISE. Further, known amounts of PSS were added to the filtrate, which were also analyzed by the ISE.

Figure 2 (b and c) shows calibration curves obtained by the method of standard addition in the PSS determination, when Workworth-coal (Australia) and Datong-coal (China) are used, respectively. These plots exhibit almost identical slopes to that of the potential response (Fig. 2, a) in the corresponding concentration range. In the case of PDCS, a result similar to that for PSS was obtained. Consequently, the concentration of the anionic polymers (PSS and PDCS) can be determined without the interference of fine coal particles or of elutriating materials from coal. This situation is very similar to that in the case of NSF determination as reported in our previous paper.³

The other dionium reagents having trimethylene chain (C_3BP) and decamethylene chain ($C_{10}BP$) were used as sensing materials, leading to results similar to that for C_6BP as shown in Table 1. The response behavior was almost independent of the added amount of supporting electrolyte (Na_2SO_4) (Table 1). This result suggests that the C_nBP -ISE correctly responds to the anionic polymer. We therefore can exclude the possibility that the ISE responds to any contaminants present in the PSS reagent such as sulfate.

When monoonium reagents, such as Capriquat and butyltrioctylphosphonium (BuMP), were used as sensing

Table 1 Response of C_nBP -ISEs to PSS

C_nBP	$[Na_2SO_4]^a/mM$	Slope ^b (mV decade ⁻¹)
C_6BP	20	21.3
C_3BP	20	24.2
$C_{10}BP$	20	21.4
C_6BP	10	23.7
C_6BP	40	20.3

a. Added as supporting electrolyte in sample solution.

b. Linear responses were obtained in a range of 2–2000 $mg\ l^{-1}$ in all cases.

materials, the ISE determination of anionic polymers (PSS and PDCS) gave a poor result; a precipitate formed during the conditioning, which was a salt between the sensing material and the anionic polymer.

A similar situation was observed in an ISE selective to naphthalenedisulfonate (NDS^{2-}) reported in our previous paper.⁶ The use of Capriquat as sensing material resulted in the formation of precipitate during conditioning, whereas by using C_6BP the determination of NDS^{2-} was effectively carried out. Consequently, ion-pair complexes between C_nBPs and polyanionic species are found to be more lipophilic than those of conventional monoonium reagents. The fact can be explained by the picture that ionic charges within the former complexes are efficiently wrapped by the alkyl chains of C_nBPs .

Recently, dionium reagents are attracting more attention as sensing materials for ISE, because of their unique selectivities compared to those of conventional monoonium reagents.^{6–8} In this work a new possibility is presented that dionium reagents can serve as sensing materials for anionic polymers, such as PSS and PDCS, and can enable us to analyze such dispersants in CWM. A detailed mechanism for the response of C_nBP -ISEs to anionic polymers is now under study.

References

1. R. L. Rowell, *Chemtech*, **1989**, 244.
2. U. Yoshimura, *Nenryo Kyokaishi*, **68**, 3 (1989).
3. A. Ohki, S. Shinkoda, K. Wakamatsu, K. Naka and S. Maeda, *Sekiyu Gakkaishi*, **34**, 452 (1991).
4. A. Ohki, M. Yamura, S. Kumamoto, S. Ide, S. Maeda and T. Takeshita, *Solvent Extr. Ion Exch.*, **7**, 57 (1989).
5. G. J. Moody and J. D. R. Thomas, "Selective Ion Sensitive Electrodes", Merrow, Watfold, Hertz, 1971.
6. A. Ohki, M. Yamura, S. Kumamoto, S. Maeda, T. Takeshita and M. Takagi, *Chem. Lett.*, **1989**, 95.
7. A. Ohki, M. Yamura, M. Takagi and S. Maeda, *Anal. Sci.*, **6**, 585 (1990).
8. V. J. Wotring, D. M. Johnson and L. G. Bachas, *Anal. Chem.*, **62**, 1506 (1990).

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