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Extraction of Organic Dianionic Species with Dicationic Extractants and Their Application to Anion Selective Electrode

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Dicationic type anion-exchange extractants, C_nBP, extracted organic dianionic species to a much greater degree as compared with classical monocationic extractants (Capriquat, etc.). This high extraction ability was applied to poly(vinyl chloride) (PVC) membrane electrode (coated-wire type). The electrode was found to be highly selective to 1,5-naphthalenedisulfonate anion (NDS^{2-}).

In recent works,[1-5] we have studied the extraction of anionic species with multi-cationic anion exchange extractants (liquid anion exchangers) such as polymethylenebis(trioctylphosphonium)s (abbreviated as C_nBP, Fig. 1). Such dicationic extractants have a higher extraction ability toward dianionic metal complexes [$M^{II}X_4^{2-}$ (M^{II}: Zn^{2+}, Cd^{2+}; X^-: Cl^-, Br^-, CN^-) and $M^{II}(C_2O_4)_2^{2-}$] in comparison with conventional monocationic extractants (e. g. methyltrioctylammonium; "Capriquat", Dojindo Lab. Ltd.). We report here the extraction of organic dianionic species with the dicationic extractants and their application to anion selective electrode.

The preparation of dicationic extractants was described in the previous paper.[5] Sodium salt of 1,5-naphthalenedisulfonate (Na_2NDS) was a commercial product and recrystallized twice from water. Other chemicals were of reagent grade and used without further purification. Extraction experiments were performed as follows. An aqueous solution (10 mL) containing organic dianion was

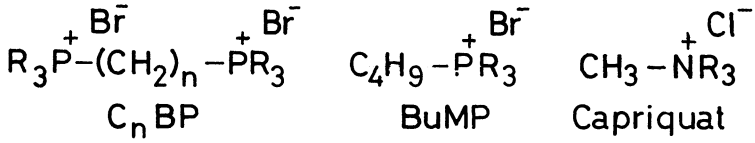

Fig. 1. Anion Exchange Extractants (R = octyl, n = 4,6,8).

shaken with an organic solution (10 mL) containing the extractant at 25 °C for 20 min. After phase separation, the concentration of the organic dianion in the aqueous phase was determined by absorption spectrophotometry or HPLC. The amount of organic dianion extracted into the organic phase was measured by back-extraction experiments as described in the previous paper.[1)]

The coated wire electrode (CWE) holding C_6BP in a PVC membrane (abbreviated as C_6BP-CWE) was prepared according to the literatures.[6,7)] The dicationic extractant (C_6BP, 120 mg) and PVC (200 mg) were dissolved into tetrahydrofuran (THF, 2 mL). In the resulting THF solution, a copper wire (1.8 mm in diameter) of coaxial cable was dipped several times to coat the wire surface with the solution uniformly, and the solvent THF was allowed to dry overnight at room temperature. The electrode was initially conditioned by soaking it in a 1 mM (1 M = 1 mol dm^{-3}) solution of NDS^{2-} for 6 h, so that the counter anion of C_6BP in the electrode membrane was converted to NDS^{2-} to be measured. In the emf measurements (at 25 °C), an Ion-meter IOC-10 (Denki Kagaku Keiki (DKK) Co.) and a DKK 4083 Ag-AgCl reference electrode were used.

Table 1 shows the extraction of some organic dianionic species with dicationic and monocationic extractants. The concentrations of monocationic extractants used in the organic phase were twice those of dicationic extractants. Therefore, there was no conditional difference of the concentration of cationic species between the extractions with dicationic and monocationic extractants.

In the extraction of NDS^{2-}, the extraction ability of dicationic extractants (C_6BP, C_8BP) was much greater than that of monocationic extractants (BuMP, Capriquat). The similar result was also obtained for the mixture of phthalate and terephthalate anions present in the aqueous phase. The favorable extraction of phthalate and terephthalate anions with C_4BP and C_8BP, respectively, suggests that the distances between two ionic centers in both the extractant and the carboxylate anions play an important role for the extractability of such dianions.

Figure 2 shows the emf response of the C_6BP-CWE to NDS^{2-} anion. The electrode

Table 1. Extraction of some organic dianions by dicationic and monocationic extractants

Dianionic species	$D^{a)}$				
	Dication			Monocation	
	C_4BP	C_6BP	C_8BP	BuMP	Capriquat
NDS^{2-} b)	0.71	2.5	2.6	0.22	0.29
Phthalate c)	0.80	0.42	0.16	0.01	0.04
Terephthalate c)	0.37	1.1	1.5	0.05	0.05

a) Distribution ratio, $D = [\text{organic anion}]_o/[\text{organic anion}]_w$.
b) Initial conditions: Aqueous phase contained 0.2 mM Na_2NDS + 20 mM NaBr, while organic phase (1,2-dichloroethane) contained an extractant (0.75 mM for dication or 1.5 mM for monocation).
c) Initial conditions: Aqueous phase contained the mixture of 0.5 mM phthalic acid and 0.5 mM terephthalic acid + 20 mM NaOH (pH > 12), while organic phase (1-octanol) contained an extractant (1.5 mM dication or 3.0 mM monocation).

exhibited a Nernstian response (29 mV decade^{-1}) in the range of 1 X 10^{-5} - 1 X 10^{-2} M NDS^{2-}.[8] This theoretical Nernstian response may indicate the formation of 1:1 ion-pair association complex $C_6BP^{2+} \cdot NDS^{2-}$ in the electrode membrane surface.

The selectivity coefficients for interference anions were determined by the mixed solution method.[9] The variation of the electrode potential was measured by changing the concentration of NDS^{2-} at the constant concentration of interference anions. The selectivity coefficients were estimated as follows: $K^{Pot}_{NDS,SO_4} < 10^{-3}$ (under the constant concentration of SO_4^{2-} (50 mM)), $K^{Pot}_{NDS,Cl} = 0.01$ (under 50 mM Cl^-), $K^{Pot}_{NDS,Br} = 0.8$ (under 10 mM Br^-). Capriquat-CWE,[10] which was prepared in a similar manner to C_6BP-CWE, showed much lower selectivity to NDS^{2-} against chloride anion ($K^{Pot}_{NDS,Cl}$ = ca. 100).

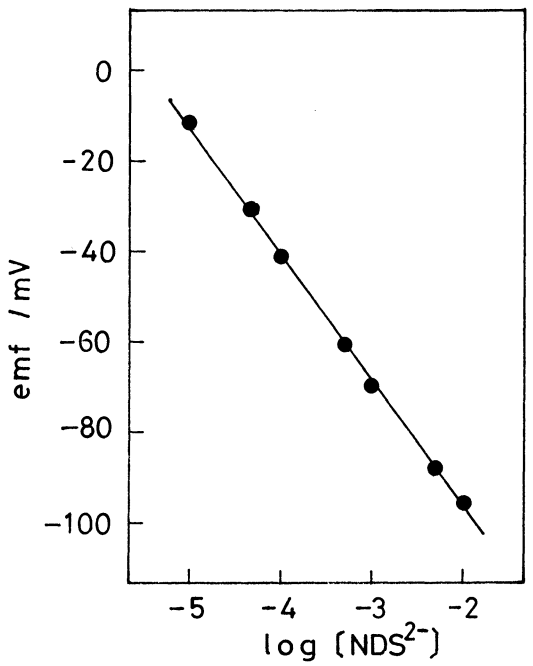

Fig. 2. Potential response of C_6BP-CWE for 1,5-naphthalenedisulfonate (NDS^{2-}) in the presence of 50 mM Na_2SO_4.

In conclusion, the high selectivity of dicationic extractants toward organic dianionic species can be effectively applied to anion selective electrode, and CWE type PVC membrane electrode with C_6BP was found to be highly selective to NDS^{2-}. In recent years, there is an increasing interest in the use of polysulfonated polynuclear aromatic compounds as a surfactant (e. g., additives for coal slurry fuels such as CWM (coal-water mixture)[11]), and so the development of a rapid and selective analytical method for such compounds becomes really required. Obviously, the idea of multi-cationic anion-exchanger may offer a new possibility in sensing organic polyanionic species by the membrane electrode.

References

1) A. Ohki, K. Dohtsu, and M. Takagi, Bunseki Kagaku, 33, E187 (1984).
2) S. Ide, A. Ohki, and M. Takagi, Anal. Sci., 1, 349 (1985).
3) A. Ohki, S. Maeda, T. Takeshita, and M. Takagi, Chem. Lett., 1987, 1349.
4) A. Ohki, X-L. Xiao, K. Tsukada, S. Maeda, and M. Takagi, Anal. Sci., 4, 143 (1988).
5) A. Ohki, M. Yamura, S. Kumamoto, S. Maeda, and T. Takeshita, Solvent Extr. Ion. Exch., in press.
6) H. James, G. Carmack, and H. Freiser, Anal. Chem., 44, 856 (1972).
7) C. R. Martin and H. Freiser, Anal. Chem., 52, 562 (1980).
8) Althogh a potential deviation (0 - 10 mV) was observed on standing the electrode in air for several days, it showed the Nernstian response in the same concentration range (10^{-5} - 10^{-2} M).
9) G. J. Moody and J. D. R. Thomas, "Selective Ion Sensitive Electrodes," Merrow Watford (1970).
10) During the soaking in the NDS^{2-} solution, white precipitate was fairly produced on the electrode surface, which may be the ion-pair between Capriquat and NDS^{2-} insoluble in the membrane phase.
11) N. Kurata, Kagaku To Kogyo, 41, 147 (1988).

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