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Preparation and Analytical Evaluation of Liquid Membrane Electrodes Based on Solid-solvents

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A new type of liquid membrane electrode has been developed in which organic compounds solidified at room temperature were used as solvents of an ion-sensing membrane. The electrode performance of a *p*-toluenesulfonate ion-sensitive electrode was examined and compared with that of a corresponding liquid membrane electrode, no remarkable difference being observed in sensitivity and response time. However, a distinct difference in selectivity was observed between the 1-octadecanol (solid) and 1-decanol (liquid) membranes. The difference was interpreted on the basis of the solvation energy of interfering anions. The effects of ion-pair concentration, membrane thickness, and pH on the electrode potentials of the 1-octadecanol membrane were investigated in comparison to those of the 1-decanol membrane. The electrodes responsive to various anions such as iodide, nitrate, bromide, and chloride were prepared with an 1-octadecanol membrane.

Liquid membrane electrodes (LME) have the advantage of a wide variety in their ion-exchanger as regards solvent extraction systems. However, they have disadvantages in practical use in comparison with solid membrane electrodes. The potentiometric response of LME is liable to be disturbed by hydrostatic pressure or stirring of the sample solution, or its ion-exchanging liquid tends to leak into the sample. In order to overcome these difficulties studies have been made resulting in the development of an LME based on plastic matrices,[1,2] carbon paste,[3] and the solidification of ion-exchanging liquid by addition of naphthalene to a nitrobenzene membrane.[4]

Organic sulfonate selective electrodes were developed by use of a coated wire type electrode.[5] We have developed a *p*-toluenesulfonate selective electrode (solid-solvent membrane electrode, SSME) using organic compounds having a high melting point, which solidify at room temperature. The effects of the membrane components, such as ion-pair concentration, membrane thickness, and pH on the response behavior of SSME with an 1-octadecanol membrane were also studied in comparison to LME with a 1-decanol membrane. The electrode performance of SSME was examined and compared with that of the corresponding LME. A distinct difference in the selectivity patterns between the 1-octadecanol (SSME) and 1-decanol (LME) membranes was observed.

Experimental

Reagents. Reagent grade solid-solvents, 1-octadecanol, 1-docosanol, *m*-dinitrobenzene, 1,2,4,5-tetrachlorobenzene and triphenyl phosphate, and liquid-solvents, 1-octanol, 1-decanol, nitrobenzene, *o*-dichlorobenzene, and tributyl phosphate were used without further purification. An ion-pair of methyltrioctylammonium *p*-toluenesulfonate (TOMA·pTS) was prepared with methyltrioctylammonium chloride (Capriquat, from Dojin Research Laboratories Co.) by the extraction method[5] and recrystallized from ethyl acetate. Capriquat salts of perchlorate, iodide, nitrate, and bromide were similarly prepared. These salts of iodide, nitrate, and bromide are hygroscopic and they were dehydrated under reduced pressure before use. The pH of the sample solution was adjusted with hydrochloric acid or sodium hydroxide solutions.

Preparation of Membranes. An ion-pair was dissolved into solid-solvent molten at elevated Temperature. After cooling at room temperature, the solidified ion-exchanger was ground into powder and pressed on a polished silver disk 1 cm in diameter at *ca.* 300 MPa to form a thin film of ion-sensing membrane. The thickness of the membranes was in the range 0.2—0.4 mm unless otherwise stated. The impedance of these membranes was several mega-ohms.

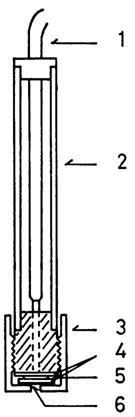

Fig. 1. Configuration of solid-solvent membrane electrode.
(1) Coaxial wire, (2) glass tube, (3) Teflon cap, (4) silver plate, (5) metal for electric conduction, and (6) pressed ion-exchanger.

Electrode Assembly and Potential Measurements. For the potentiometric test of the pressed membranes, SSME was constructed as shown in Fig. 1. For LME, a Corning type liquid membrane electrode was used. The membrane potentials were measured *versus* SCE with an Orion Digital Ionalyzer Model 601 connected to a Matsushita pen recorder Model VP654A.

Results and Discussion

The membrane conditions which affect the electrode response of SSME with an 1-octadecanol membrane responsive to *p*-toluenesulfonate ion (pTS) were investigated in comparison to those of LME with a 1-decanol membrane as follows:

Effect of the Ion-pair Concentration. Dependence of the sensitivity of the SSME on the concentration of the ion-pair is illustrated in Fig. 2. The optimum concen-

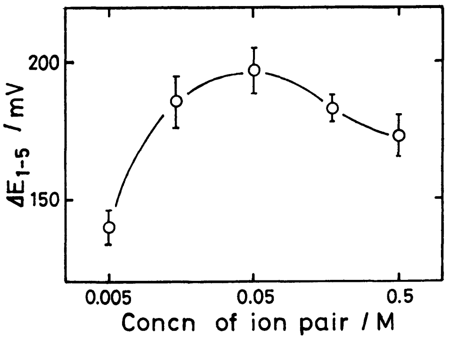

Fig. 2. Effect of ion-pair concentration on the potential difference between 10^{-1} M and 10^{-5} M.
Ion-exchanger: TOMA·pTS in 1-octadecanol (20 mg). The mean value of four measurements with its standard deviation is given.

tration of the ion-pair is *ca.* 0.05 M†. As in LME,[6] the sensitivity decreased in a very high concentration region due to the elution of the membrane solute. The sensitivity decreased also in low concentration range, the membrane potential becoming unstable below 0.005 M because of the increase of membrane impedance. The potential reproducibility of SSME was not very good, ±5 mV, in comparison to the conventional liquid membrane electrode.

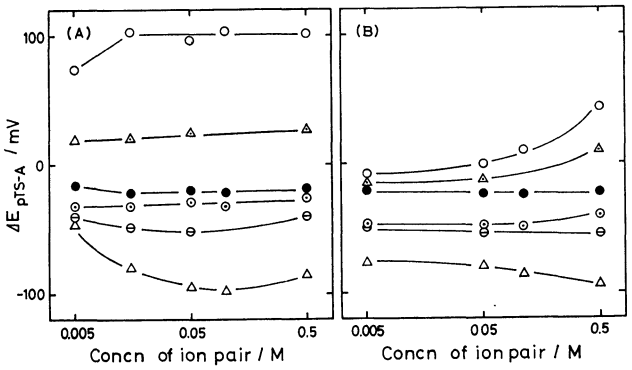

Fig. 3. Effect of ion-pair concentration on SPD of (A) SSME and (B) LME.
Interfering ions: (○) ClO_4^-, (△) I^-, (●) $PhSO_3^-$, (⊙) NO_3^-, (⊖) Br^-, and (△) Cl^-.

The selectivity of SSME changes slightly with the concentration of the ion-pair (Fig. 3A). Selective potential difference (SPD, $\Delta E_{\text{pTS-A}}$) was defined in order to study the selectivity characteristic of the membrane as follows. The membrane potentials of 0.01 M objective pTS ion (E_{pTS}) and each interfering anion (E_{A}) were measured separately. The potential difference, $\Delta E_{\text{pTS-A}}=E_{\text{pTS}}-E_{\text{A}}$, was used instead of the conventional selectivity factor because of its super-Nernstian responses. The decrease in selectivity at 0.005 M resulted from the poor response to the objective ions. On the other hand, the range of the selectivity of LME widened somewhat with increase in concentration of the ion-pair (Fig. 3B).

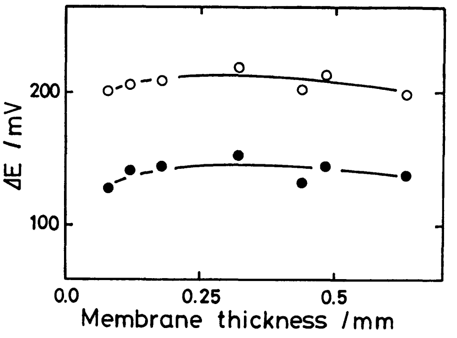

Fig. 4. Effect of membrane thickness on the potential defference between 10^{-1} M and (●) 10^{-4} M or (○)10^{-5} M.
Ion-exchanger: 0.05 M TOMA·pTS in 1-octadecanol.

Effect of the Membrane Thickness. As shown in Fig. 4, the sensitivity of the SSME is not influenced much by the membrane thickness, little effect of the membrane thickness on selectivity and response time being observed.

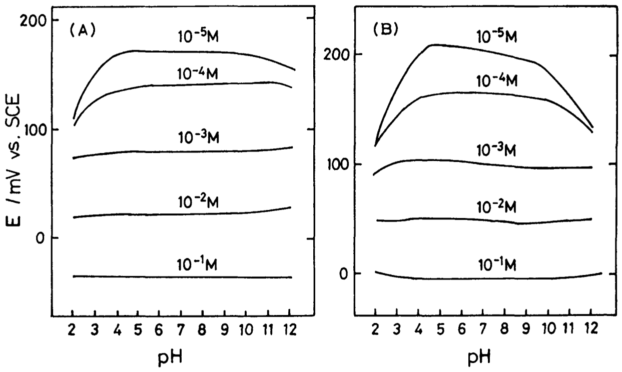

Fig. 5. Effect of pH on the membrane potentials of (A) SSME and (B) LME.
Ion-exchanger: 0.05 M TOMA·pTS in (A) 1-octadecanol and (B) 1-decanol.

Effect of pH. The effects of pH on the membrane potential of SSME (A) and LME (B) were examined (Fig. 5). In the low pH range, the interference of chloride ion could not be ignored in both membranes, the interference of hydroxide ion in an alkaline solution being much larger in LME than in SSME.

Comparison of the Potentiometric Behavior of SSME with That of LME. The response behavior of SSME and LME is summarized in Table 1, four pairs of the pressed membranes and the corresponding liquid membranes being compared. Super-Nernst slopes were observed for both liquid and pressed membranes. This might be attributed to the malfunction of the reference electrode as reported by Moody and Thomas.[7] SSME gave a slightly better result in the linear response ranges in comparison to the corresponding LME except in the case of a pair of 1-alkanols. Since the linear response range of LME depends not only on the membrane solvent but also on the ion-pair species,[6] the most appropriate solvent for a given ion-pair should be selected in order to obtain a highly sensitive electrode. In view of the wide linear response range, 1-decanol

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† Throughout this paper 1 M=1 mol dm^{-3}.

TABLE 1. RESPONSE BEHAVIOR OF *p*-TOLUENESULFONATE ION-SENSITIVE ELECTRODES WITH (A) LIQUID MEMBRANE AND (B) SOLID-SOLVENT MEMBRANE

Solvent	Mp / °C	Type of membrane	Slope / mV/pa	Limit of linear response/pa	Response time/min at 10^{-2} M	Response time/min at 10^{-4} M
1-Decanol	7	A	64.2	3.8	1.2	4.6
1-Octadecanol	59	B	64.7	3.7	2.0	3.7
Nitrobenzene	6	A	66.1	3.4	1.0	4.1
m-Dinitrobenzene	90	B	62.9	3.6	0.5	3.4
o-Dichlorobenzene	−17	A	63.4	3.4	1.6	2.7
1,2,4,5-Tetrachlorobenzene	140	B	67.1	3.6	0.1	2.5
Tributyl phosphate	−80	A	62.1	3.4	1.6	2.3
Triphenyl phosphate	49	B	67.9	3.7	0.1	2.4

Ion-pair: *ca.* 0.1 M TOMA·pTS, Temp: 25 °C.

was found to be the best liquid-solvent of those tested for a long chain tetraalkylammonium as a counter ion. However, in case of SSME, the linear response range was independent of the kind of solid-solvent used. The sensitivity of SSME seems to be determined mainly by the solubility of the ion-pair.[8] Shorter response time was needed for SSME than the corresponding LME, especially in the high concentration range of pTS^-.

The selectivity characteristics of SSME and LME based on various solvents are shown in Figs. 6 and 7. Hardly any difference was observed among the solid-solvents in the selectivity patterns of SSME (Fig. 6A), while an exceptional pattern was found among LME for 1-decanol membrane (Fig. 6B).

The selectivity patterns of SSME with solid 1-alkanols were compared with those of LME with liquid 1-alkanols (Fig. 7). A distinct difference in patterns was observed. The solvent effects of the solid-solvents on the selectivity pattern were small in contrast to the liquid-solvents examined. The potentials of SSME seem to be governed mainly by the direct ion-exchange reaction at the membrane-solution interface, being hardly affected at all by the inner-membrane phenomena. The selectivity of SSME was anticipated to be determined mainly by the hydration energy of the interfering ions. A linear relationship is seen between hydration energy and the SPD for an 1-octadecanol membrane, no such correlation being observed for a 1-decanol membrane (Fig. 8). The SPD of the 1-decanol membrane seems to be determined not only by the hydration energy of interfering anions but also

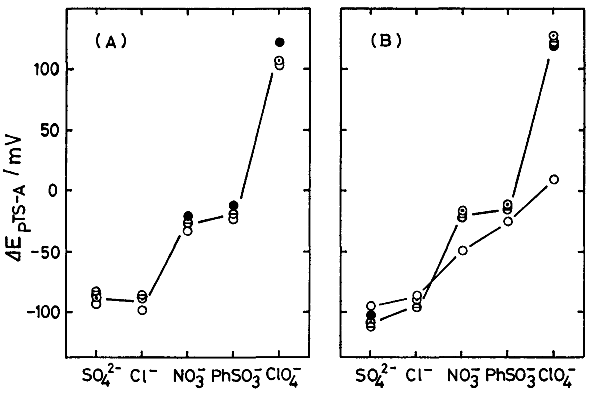

Fig. 6. Selectivity patterns of (A) SSME and (B) LME. Solvents used for SSME: (●) triphenyl phosphate, (⊙) *m*-dinitrobenzene, (⊖) 1,2,4,5-tetrachlorobenzene, and (○) 1-octadecanol.
Solvents used for LME: (●) tributyl phosphate, (⊙) nitrobenzene, (⊖) *o*-dichlorobenzene, and (○) 1-decanol.

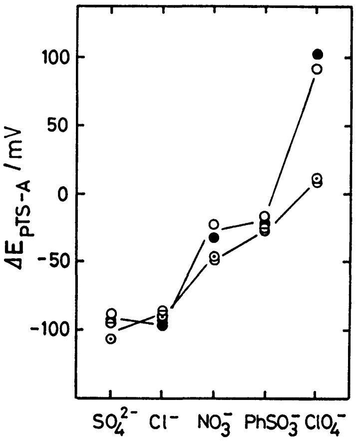

Fig. 7. Selectivity patterns of (●) 1-octadecanol, (○) 1-docosanol, (⊙) 1-octanol, and (⊖) 1-decanol membranes.

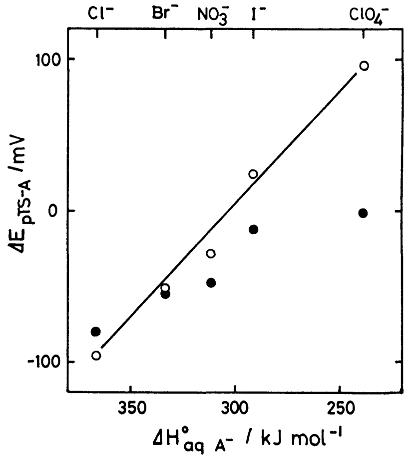

Fig. 8. Relationship between standard hydration enthalpy and SPD. (○) 1-Octadecanol and (●) 1-decanol membranes.

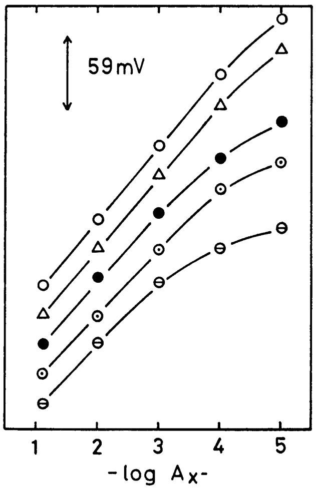

Fig. 9. Calibration curves of solid-solvent membranes. Ion-exchanger: 0.05 M TOMA·X^- in 1-octadecanol (20 mg).
X^-: (○) ClO_4^-, (△) I^-, (●) NO_3^-, (⊙) Br^-, and (⊖) Cl^-.

by the solvation energy in the solvent, as reported by Reinsfelder and Schults for the $Fe(bphen)_3^{2+}$–*t*-pentyl alcohol electrode.[9]

SSMEs Responsive to Other Anions. Figure 9 shows the calibration curves of each electrode sensitive to the respective anions. The sensitivity to ions having a smaller hydration energy is better than that having a larger one.[8,10] SSME with 1-octadecanol membrane has several merits over LME with common aromatic compounds; 1) it is insoluble in water, 2) it does not sublime, and 3) it can be use as the matrix of a coated-wire type electrode in place of the conventional PVC matrix.

An SSME with an inner reference electrode showed reproducibility to be better than ±2 mV. This type of pressed membrane should be *ca.* 0.5 mm thick or else it will break easily. A coated-wire type SSME, prepared by dipping a platinum tip into the extract of the ion-pair in molten 1-octadecanol, also showed good response.

SSME has advantages of both solid and liquid membranes; it shows fast response and can be used as a sensor of a flowing system.[11] The contamination of the sample solution with the eluted solvent from the membrane can be minimized. It is widely applicable to most LME-systems. A highly selective organic sulfonate ion selective electrode with alkylphenol derivative has been developed.[12]

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