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On the Enhancement of the Selectivity of Organic Sulfonate Ion Electrode by Alkylphenols[†]

Hirokazu Hara, Satoshi Okazaki, and Taitiro Fujinaga*
Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606

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An enhancing effect of alkylphenols on the selectivity of the liquid membrane electrode responsive to organic sulfonate ion has been investigated. The interference of perchlorate ion expressed in terms of the selectivity coefficient decreased to one eighthundredth in the presence of *p-t*-octylphenol. This effect was attributed to the formation of the hydrogen bonding between the phenol and sulfonate. The dependence of the potentiometric behavior, paticularly with respect to the selectivity on the membrane components was examined. The optimum composition of the ion-exchanger for sulfonate was found to be 0.05 mol dm^{-3} trioctylmethylammonium *p*-toluenesulfonate with 0.5 mol dm^{-3} *p-t*-octylphenol in *o*-dichlorobenzene. The decrease of the selectivity coefficient for perchlorate due to the phenol was also discussed in relation to ion-exchange equilibrium constants, ionic parameters, and dissociation constants of the ion-pair. The effect of the membrane solvents was also discussed in terms of their solubility parameters.

To date, in a liquid membrane electrode, more interest has been shown in the membrane solvent rather than in the ion-exchange site as an effectual dominant of selectivity. Though several useful solvents having wide selectivity ranges, such as nitrobenzene and 1,2-dichloroethane have been recommended,[1,2] the selectivity of the liquid membrane electrode is generally insufficient. Particularly, in the case of an anion sensitive electrode, an ion-exchanger such as a neutral carrier for cation selective electrode has not been developed.

In the previous papers,[3,4] the authors have reported on an organic sulfonate ion selective electrode of a coated wire type and a solid solvent membrane type. In the course of the study on the selectivity characteristics of *p*-toluenesulfonate (pTS) ion selective electrode, the authors found an enhancing effect of an alkylphenol on the selectivity, *i.e.*, the interferences of the inorganic anions such as perchlorate, tetrafluoroborate ions decreased remarkably by the addition of some alkylphenols into the liquid membrane; for example, the logarithmic selectivity coefficient of perchlorate decreased from +2.3 to −0.6 in the presence of 0.5 M[††] *p-t*-octylphenol(*p*-(1,1,3,3-tetramethylbutyl)phenol; ptOP). This effect of the phenol was attributed to the formation of hydrogen bonding between the phenol and pTS anion.

In this paper, the influences of the concentration of ion-pair and phenols upon the membrane response and selectivity were examined. This phenomenon was interpreted on the basis of Sandblom-Eisenman-Walker theory.[5] The effect of some alkylphenols on the selectivity was studied in relation to their hydrogen bonding ability. The effect of the membrane solvents was also discussed with reference to their hydrogen bonding parameters.

Experimental

Reagents. All chemicals were of analytical reagent grade and used without further purification unless otherwise noted. Ion-pair of trioctylmethylammonium(abbreviated as TOMA) with *p*-toluenesulfonate was synthesized as follows: trioctylmethylammonium chloride (commercially available as Capriquat from Dojin Chemicals, Kumamoto) dissolved in chloroform was shaken with an aqueous solution of 0.1 M sodium pTS for 10 min. The extraction was repeated several times until chloride was not detected any more in the aqueous phase. After chloroform was evaporated by a rotary evaporator, the deposit was recrystallized from ethyl acetate. *o*-Dichlorobenzene used for the conductivity measurements was purified by distillation after the dehydration with calcium hydride. Its water content was estimated as 0.02% (v/v) by gas chromatography. A series of the following phenols were examined: *p-t*-octylphenol (*p*-(1,1,3,3-tetramethylbutyl)phenol; ptOP), *p-t*-pentylphenol (ptPP), *p-t*-butylphenol (ptBP) 2,3,5-trimethylphenol, 2,4,6-trimethylphenol, and 2,6-di-*t*-butyl-4-methylphenol.

Preparation of Membranes. A liquid membrane was prepared by dissolving the ion-pair of TOMA pTS into *o*-dichlorobenzene, which was held in a Corning probe with a hydrophobic ceramic junction. A solid solvent membrane[4] was prepared by dissolving the ion-pair in phenol at elevated temperature and then powdered. *Ca.* 30 mg of the ion-exchanger was pressed at a pressure of 3×10^8 Pa on a silver disk of 1 cm in diameter. The electrical contact was taken directly from the silver disk.

Apparatus. Membrane potentials were measured against SCE at 25 °C with an Orion Digital Ionalyzer Model 601 equipped with a Matsushita Pen Recorder Model VP654-A. IR spectra were measured by a JASCO Infrared Spectrophotometer Model DS-402G using a NaCl cell having a light pass length of 0.1 mm. The conductivity was measured at 25 °C by a Yokogawa Universal Bridge Type BV-Z-13B with a cell having a cell constant of 0.1060 s cm^{-1}.

Estimation of Various Parameters. Logarithmic selectivity coefficient, log K^{pot} was measured by the separate solution method; the potential difference between a solution of 10^{-2} M pTS$^-$ and that of interfering anion was divided by the slope of the calibration curve for pTS$^-$. For the measurement of ion-exchange equilibrium constant, K^{ex}, 50 cm^3 of 10^{-2} M organic solution of TOMA pTS was shaken with the equivolume of 10^{-2} M aqueous solution of sodium perchlorate for 1 h at 25 °C. After the ion-exchange equilibrium in Eq. 1 was reached,

$$(\text{TOMA pTS})_{\text{org}} + (\text{ClO}_4^-)_{\text{aq}} \overset{K^{\text{ex}}}{\rightleftharpoons} (\text{TOMA ClO}_4)_{\text{org}} + (\text{pTS}^-)_{\text{aq}}, \qquad (1)$$

[†] A preliminary report has been published: T. Fujinaga, S. Okazaki, and H. Hara, *Chem. Lett.*, **1978**, 1201.

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

$$K^{\mathrm{ex}} = \frac{[\mathrm{TOMA\ ClO_4}]_{\mathrm{org}}[\mathrm{pTS^-}]_{\mathrm{aq}}}{[\mathrm{TOMA\ pTS}]_{\mathrm{org}}[\mathrm{ClO_4^-}]_{\mathrm{aq}}}, \qquad (2)$$

the concentrations of $\mathrm{pTS^-}$ and $\mathrm{ClO_4^-}$ in the aqueous phase were measured with the liquid membrane electrodes, the ion-exchanger of which were TOMA pTS plus ptOP and TOMA $\mathrm{ClO_4}$ in *o*-dichlorobenzene for *p*-toluenesulfonate and perchlorate electrodes, respectively. For the associated ion-pair, the mole fractions of ions extracted in the organic phase were assumed to be equal to those of ions eluted inversely into the aqueous phase. Thus, after the equilibrium was reached, following relationships hold; $[\mathrm{TOMA\ pTS}]_{\mathrm{org}}=[\mathrm{ClO_4^-}]_{\mathrm{aq}}$, $[\mathrm{TOMA\ ClO_4}]_{\mathrm{org}}=[\mathrm{pTS^-}]_{\mathrm{aq}}$. Then, Eq. 2 is simplified as follows,

$$K^{\mathrm{ex}} = [\mathrm{pTS^-}]^2_{\mathrm{aq}}/[\mathrm{ClO_4^-}]^2_{\mathrm{aq}}. \qquad (2)'$$

The molar conductivities of $\mathrm{ClO_4^-}$ and $\mathrm{TOMA^+}$ at infinite dilution were obtained using tetrabutylammonium tetraphenylborate as a reference electrolyte.[6] The dissociation constant, K^{D} of TOMA $\mathrm{ClO_4}$ in the absence of ptOP was estimated by the Shedlovsky method.[7] Being considered small the interactions between the phenol and $\mathrm{TOMA^+}$ or $\mathrm{ClO_4^-}$, the molar conductivity of $\mathrm{TOMA^+}$, $\lambda^\circ(\mathrm{TOMA^+})_{\mathrm{p}}$ in the presence of ptOP, was assumed to have the same magnitude as that in the absence of the phenol. Also $\lambda^\circ(\mathrm{ClO_4^-})_{\mathrm{p}}$ was estimated so that the K^{D} values in the presence and absence of the phenol were of the same magnitude. Here, K^{D} in the presence of the phenol was calculated by Eq. 3,

$$K^{\mathrm{D}} = C(\Lambda/\Lambda_0)^2/(1-\Lambda/\Lambda_0), \qquad (3)$$

where Λ is the conductivity at the concentration $C(10^{-5}\ M < C < 10^{-4}\ \mathrm{M})$ and Λ_0 is the molar conductivity given by the sum of $\lambda^\circ(\mathrm{TOMA^+})_{\mathrm{p}}$ and $\lambda^\circ(\mathrm{ClO_4^-})_{\mathrm{p}}$. The $\lambda^\circ(\mathrm{pTS^-})$ and $\lambda^\circ(\mathrm{pTS^-})_{\mathrm{p}}$ were obtained assuming that Walden's rule holds in these systems,[8] *i.e.*,

$$\lambda^\circ(\mathrm{pTS^-}) = 0.7 \times \lambda^\circ(\mathrm{ClO_4^-}),$$

$$\lambda^\circ(\mathrm{pTS^-})_{\mathrm{p}} = 0.7 \times \lambda^\circ(\mathrm{ClO_4^-})_{\mathrm{p}}. \qquad (4)$$

The dissociation constants for TOMA pTS were calculated from Eq. 3 using these relations.

The formation constants, K^{F}_1 between $\mathrm{pTS^-}$ and alkylphenols were estimated according to the method reported by Aitken and Gilkerson.[9] The dissociation constant, K^{D} for TOMA pTS in the absence of a phenol is assumed to be given in Eq. 3. If the dissociation constant varies from K^{D} to $K^{\mathrm{D}}_{\mathrm{p}}$ by the addition of phenol, then,

$$K^{\mathrm{D}}_{\mathrm{p}}/K^{\mathrm{D}} = (C_{\mathrm{p}}/C)(\Lambda_{\mathrm{p}}/\Lambda_{0\mathrm{p}})^2(\Lambda/\Lambda_0)^{-2}(1-\Lambda/\Lambda_0) \times (1-\Lambda_0/\Lambda_{0\mathrm{p}})^{-1}. \qquad (5)$$

This equation can be reduced to Eq. 6, provided that the concentration of ion-pair is constant, *i.e.*, $C_{\mathrm{p}}=C$, and the molar conductivities Λ and Λ_{p} at concentration C and C_{p} are much smaller than those at infinite dilution.

$$K^{\mathrm{D}}_{\mathrm{p}}/K^{\mathrm{D}} = (\Lambda_{\mathrm{p}}/\Lambda)^2 \equiv R \qquad (6)$$

Those simplifying assumptions are reasonable in a solvent of low dielectric constant such as *o*-dichlorobenzene. The following interactions were assumed to exist between $\mathrm{pTS^-}$ or ion-pair and the phenol (denoted by P),

$$\mathrm{pTS^-} + \mathrm{P} \rightleftharpoons \mathrm{pTS{\cdot}P^-},\ K^{\mathrm{F}}_1 = [\mathrm{pTS{\cdot}P^-}]/[\mathrm{pTS^-}][\mathrm{P}] \qquad (7)$$

$$\mathrm{TOMA\ pTS} + \mathrm{P} \rightleftharpoons \mathrm{TOMA\ pTS{\cdot}P},$$

$$K^{\mathrm{F}}_2 = [\mathrm{TOMA\ pTS{\cdot}P}]/[\mathrm{TOMA\ pTS}][\mathrm{P}]. \qquad (8)$$

Then the ratio, $K^{\mathrm{D}}_{\mathrm{p}}/K^{\mathrm{D}}$ was given by Eq. 9,[9,10]

$$K^{\mathrm{D}}_{\mathrm{p}}/K^{\mathrm{D}} = (1+K^{\mathrm{F}}_1[\mathrm{P}])/(1+K^{\mathrm{F}}_2[\mathrm{P}]). \qquad (9)$$

The lefthand side of Eq. 9 is approximated by R and the righthand side by $(1+K^{\mathrm{F}}_1[\mathrm{P}])$ at low concentration of the phenol. Consequently, K^{F}_1 can be obtained from the slope of the plot of R *vs.* [P].[9]

Results and Discussion

Effect of ptOP on the Sensitivity and Selectivity. The effects of the concentrations of the ion-pair, TOMA pTS and the phenol on the sensitivity and selectivity of the sulfonate electrode were examined. The potential difference between the $\mathrm{pTS^-}$ solutions of 10^{-1} M and 10^{-5} M was defined as a sensitivity factor, $\Delta E_{1\text{-}5}$. In the absence of the phenol, both the sensitivity and selectivity were independent of the ion-pair concentration over the experimental range from 1.5 mM to 50 mM; *i.e.*, $\Delta E_{1\text{-}5}\approx 200$ mV and $\log K^{\mathrm{pot}}\approx 2.3$, 0.6, -0.5, -1.0, and -2.0 for perchlorate, iodide, nitrate, bromide, and chloride ions, respectively. When the concentration of the ion-pair was below 0.5 mM, the sensitivity decreased to 170 mV, owing to the decrease of the ion-exchange current density due to the dilution of the ion-exchanger. In the case of the diluted ion-exchanger membrane, as shown in Fig. 1-a, the values of $\log K^{\mathrm{pot}}$ were decreased in proportion to the logarithm of the ptOP concentration and also the value $\Delta E_{1\text{-}5}$ was decreased more significantly. When the concentration of the ion-pair was sufficiently high, the membrane maintains still high sensitivity even at high concentration of ptOP, as shown in Fig. 1-b. In conclusion, the optimum concentration of ptOP was chosen at 0.5 M. Figure 2 shows the relationships between the concentration of the ion-pair and the sensitivity factor or logarithmic selectivity coefficients in the presence of 0.5 M

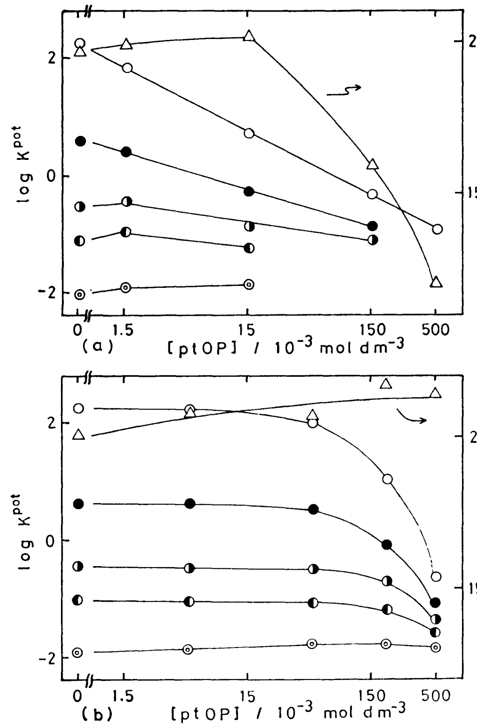

Fig. 1. Effect of concentration of *p-t*-octylphenol on selectivity coefficients and sensitivity factor $\Delta E_{1\text{-}5}$.
(a): $[\mathrm{TOMA\ pTS}]=1.5\times10^{-3}\ \mathrm{mol\ dm^{-3}}$, (b): $[\mathrm{TOMA\ pTS}]=50\times10^{-3}\ \mathrm{mol\ dm^{-3}}$.
○ $\mathrm{ClO_4^-}$, ● $\mathrm{I^-}$, ◑ $\mathrm{NO_3^-}$, ◐ $\mathrm{Br^-}$, ◎ $\mathrm{Cl^-}$.

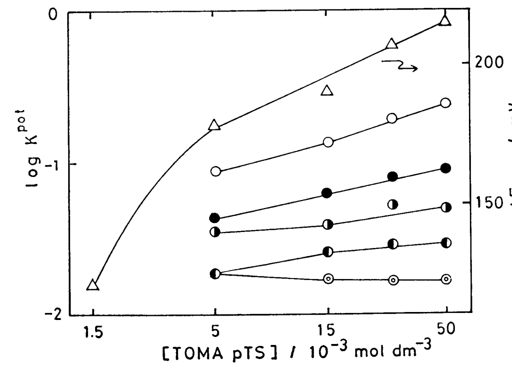

Fig. 2. Effect of concentration of TOMA pTS on selectivity coefficients and sensitivity factor $\Delta E_{1\text{-}5}$. [ptOP]=0.5 mol dm^{-3}, ○: ClO_4^-, ●: I^-, ◑: NO_3^-, ◐: Br^-, ◎: Cl^-.

ptOP. The concentration of the ion-pair should be higher than 0.03 M to keep the sensitivity sufficiently high.

As shown in Figs. 1 and 2, the interference of perchlorate decreased remarkably by the addition of ptOP, though perchlorate is one of the most serious interferent against the conventional liquid membrane electrodes. It seems to be noteworthy that the selectivity coefficient for perchlorate is reduced to one eight-hundredth and becomes smaller than one, in other words, perchlorate becomes a "weaker" anion than pTS anion. This remarkable change in selectivity against perchlorate by ptOP can be explained on the basis of Sandblom-Eisenman-Walker theory[5,11] for the liquid membrane potential. In the case of a strongly associated ion-pair, the membrane potential E is given by Eq. 10[11]

$$\frac{F}{RT}E = (1-\tau)\ln\frac{a_i'+\bar{P}a_j'}{a_i''+\bar{P}a_j''} + \tau\ln\frac{a_i'+\bar{K}a_j'}{a_i''+\bar{K}a_j''}, \quad (10)$$

where a_i', a_j', a_i'', and a_j'' are activities of ions i and j in the phases denoted with suffixes (′) and (″). Three selectivity factors $\bar{P}$, $\bar{K}$, and τ are defined by Eqs. 11—13;

$$\bar{P} = \frac{(u_j+u_s)k_j}{(u_i+u_s)k_i} = \frac{u_j+u_s}{u_i+u_s}K^{ex}\frac{K_{js}^D}{K_{is}^D}, \quad (11)$$

$$\bar{K} = \frac{u_{js}}{u_{is}}K^{ex}, \quad (12)$$

$$\tau = \frac{u_s[(u_{js}/K_{js}^D)-(u_{is}/K_{is}^D)]}{(u_i+u_s)(u_{js}/K_{js}^D)-(u_j+u_s)(u_{is}/K_{is}^D)}\ (0<\tau<1), \quad (13)$$

where u_i, u_j, u_{is}, u_{js} are the mobilities of ions i, j, and ion-pairs in liquid membrane, k_i and k_j are the partition coefficients and K_{is}^D K_{js}^D, are the ion-pair dissociation constants and K^{ex} is the ion-exchange equilibrium constant. Therefore, $\bar{P}$ is governed by the mobilities of ions in the membrane and their partition equilibria, whereas $\bar{K}$ is governed by the mobilities of the ion-pair and the ion-exchange equilibrium constant of Eq. 1. A parameter τ indicates the relative weight between $\bar{P}$ and $\bar{K}$, and depends on the ion dissociation phenomena in the membrane. These parameters estimated with respect to ions pTS$^-$(i) and ClO_4^-(j) in the presence and absence of ptOP are summarized in Table 1 together with the potentiometric selectivity constant, K^{pot}.

The observed selectivity coefficients in the presence and absence of ptOP agree fairly well with the mean values between $\bar{P}$ and $\bar{K}$. This indicates that the variation of the selectivity coefficient can be interpreted well by this theory. The factors of the mobility ratio and the dissociation constant ratio in Eqs. 11 and 12 vary at most three times by the addition of ptOP. Therefore, it seems that these factors are not responsible for the lowering of the selectivity of perchlorate. Judging from the variation of τ caused by the addition of ptOP, the contribution of the associated species to the selectivity is large in the absence of ptOP, whereas the contribution of the diffusion of free ions becomes important in the presence of ptOP, namely, this variation results from

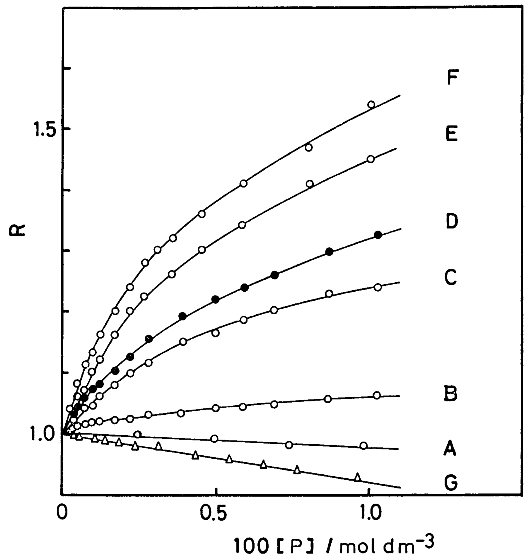

Fig. 3. R *vs.* [P] plots for alkylphenols.
10^{-4} mol dm^{-3} TOMA pTS+alkylphenol in *o*-dichlorobenzene.
(A): 2,6-Di-*t*-butyl-4-methylphenol, (B): 2,4,6-trimethylphenol, (C): 2,3,5-trimethylphenol, (D): *p*-*t*-octylphenol, (E): *p*-*t*-pentylphenol, (F): *p*-*t*-butylphenol, (G): 10^{-4} mol dm^{-3} TOMA ClO_4+*p*-*t*-octylphenol.

TABLE 1. EFFECTS OF ptOP ON THE SELECTIVITY PARAMETERS OF TOMA pTS/*o*-DICHLOROBENZENE MEMBRANE

Solvent	K^{pot}	τ	$\bar{P}$	$\bar{K}$	λ_s°	λ_i°	λ_j°	K_{is}^D ($\times 10^{-6}$)	K_{js}^D ($\times 10^{-6}$)	K^{ex}
o-Dichlorobenzene										
without PtOp	200[a)]	0.69	520	60	9.9	17.2	24.6	1.1	8.5	53
with 0.5 M ptOP	0.25[a)]	0.44	0.26	0.11	9.9	7.1	10.1	3.5	8.6	0.091

Subscript i, j, and s refer to pTS$^-$, ClO_4^-, and TOMA$^+$, respectively. a) Concentration of ion-pair is 0.05 M.

the promotion of the dissociation of ion-pair by the formation of hydrogen bonding between the ptOP and sulfonate.

Relationship between the Hydrogen Bonding Abilities of Alkylphenols and Selectivity of Sulfonate Electrode. As a measure of the hydrogen bonding abilities of alkylphenols used, the formation constants, K_1^F between pTS$^-$ and the phenols were evaluated from the slopes of the extrapolation of the plot of R *vs.* [P] back to the zero concentration of the phenols, as shown in Fig. 3. In the figure, when the concentration of the phenols becomes high, the plots are curving convexly. This indicates the formation of the associated species between the phenols and the ion-pair. It can be seen in the Figure, that the more sterically hindered the hydroxyl group of the phenols is, the smaller the K_1^F value becomes (A—D). The phenols having small *p*-alkyl substituent were likely to show the large values of K_1^F (D—F). This result does not necessarily indicate that the hydrogen bonding ability increases in the order, D<E<F in *p*-alkyl-substituted phenols, because the molar conductivities of the associated species between pTS$^-$ and these phenols vary with their sizes. Namely, the larger the phenol is, the more slowly the associated species move. In the case of TOMA ClO_4 (curve G), the decrease of R was observed. The result is explained that only the free perchlorate anion is associated with ptOP and the molar conductivity of the associated species decreases in comparison with that of the free perchlorate.

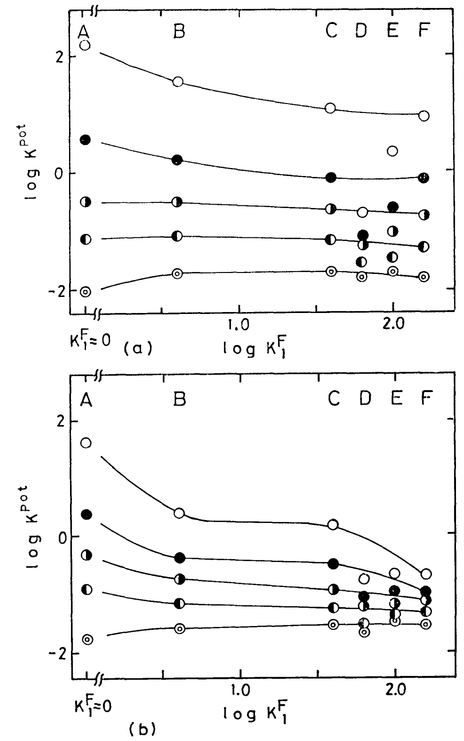

Fig. 4. Relationship between formation constant and selectivity coefficients.
(A)—(F): Same as in Fig. 3.
(a): Liquid membrane (0.03 mol dm^{-3} TOMA pTS+ 0.5 mol dm^{-3} ptOP in *o*-dichlorobenzene), (b): Solid solvent membrane (0.05 mol dm^{-3} TOMA pTS in alkylphenol).

These results obtained by conductometry were confirmed by the IR spectra of these phenols in *o*-dichlorobenzene in the presence of pTS$^-$ or ClO_4^-. The stretching band ν(OH) of phenols near 3600 cm^{-1} shifted to the longer wavelength by the addition of pTS$^-$, the shift of which was in proportion to the hydrogen bonding abilities of the phenols with sulfonate.[12,13] As shown in Table 2, a good correlation was obtained between the frequency shift of the ν(OH) band and the formation constants measured by conductmetry (A—D). The difference was not entirely observed among the hydrogen bonding abilities of the *p*-alkyl-substituted phenols (D—F), in spite of the remarkable difference in their formation constants. The shift of the ν(OH) band was also observed when ptOP was added to the solution of TOMA ClO_4, and this shift shows the formation of associated species between ptOP and perchlorate. Figure 4 shows the relationships between log K^{pot} and log K_1^F with respect to the liquid membrane (upper) and to the solid solvent membrane (lower), respectively. It can be said that the more sterically hindered the phenols are, the less selective the electrode is in both the liquid and solid solvent membranes (A—C,F). The effect of the size of *p*-alkyl substituent was significant in the liquid membrane in contrast with the solid solvent membrane (D—F). This result can be explained by the fact that in the liquid membrane the surface concentration of the phenols decreased with decreasing the size of *p*-alkyl substituent by the dissolution of phenol into the aqueous phase. Consequently, the highest selectivity was observed with ptOP having the largest *p*-alkyl substituent among the phenols D,E,F. The lowering tendency of the selectivity in the liquid membrane in comparison with that in the solid solvent membrane can be interpreted in the same way.

Effect of the Membrane Solvents on the Selectivity. The solvent effect on the selectivities of the sulfonate electrode was examined in the presence and absence of ptOP. Jyo *et al.*[2] examined the solvent effects in the liquid membrane electrode and reported that chloroform enhanced the selectivity for halide ion and 1-decanol decreased the selectivity of perchlorate and

TABLE 2. COMPARISON BETWEEN INFRARED FREQUENCY SHIFT OF ALKYLPHENOLS AND LOGARITHMIC FORMATION CONSTANT

Phenol	2,6-Di-*t*-butyl-4-methylphenol	2,4,6-Tri-methylphenol	2,3,5-Tri-methylphenol	ptOP	ptPP	ptBP
$\Delta\nu$(OH)$^{a)}$ cm^{-1}	0	330	380	400	400	400
log K_1^F $^{b)}$	—$^{c)}$	0.6	1.6	1.8	2.0	2.2

a) Frequency shift caused by pTS$^-$ in *o*-dichlorobenzene. b) Formation constant between pTS$^-$ and phenol measured by conductometry. c) No formation was observed.

Table 3. Solvent effects on the selectivity coefficients in the presence and absence of ptOP
Ion-exchanger: 0.05 M TOMA pTS without(or with 0.5 M) ptOP in each solvent.

Solvent	δ_h[a] ($MPa^{1/2}$)	log K^{pot}											
		ClO_4^-	BF_4^-	SCN^-	RSO_3^-[b]	I^-	ClO_3^-	ϕSO_3^-	NO_3^-	Br^-	NO_2^-	BrO_3^-	Cl^-
o-Dichlorobenzene	3.3	2.3	1.6[c]	1.2	1.1	0.6	−0.2	−0.3	−0.4	−1.0	−1.3	−1.5	−1.9
with 0.5 M ptOP	—	−0.6	−1.2[c]	−0.3	0.8	−1.1	−1.5	−0.5	−1.3	−1.5	−1.2	−2.0	−1.8
Nitrobenzene	4.1	2.0	1.4	1.1	0.8	0.7	−0.1	−0.3	−0.2	−0.8	−1.0	−1.1	−1.6
with 0.5 M ptOP	—	0.0	−0.6	0.1	0.7	−1.0	−1.3	−0.5	−1.0	−1.4	−1.1	−1.8	−1.7
Chloroform	5.7	1.8	1.1	1.1	1.0	1.1	−0.1	−0.3	−0.3	−0.6	−1.2	−1.2	−1.5
with 0.5 M ptOP	—	−0.7	−1.2	−0.3	0.7	−0.9	−1.3	−0.5	−1.1	−1.4	−1.1	−1.6	−1.6
1-Octanol	11.9	0.1	−0.5	0.3	0.7	−0.2	−0.8	−0.5	−0.9	−1.0	−1.2	−1.7	−1.5
with 0.5 M ptOP	—	−0.3	−0.9	0.1	0.7	−0.5	−1.0	−0.5	−1.0	−1.1	−1.1	−1.7	−1.5

a) Hydrogen bonding component of solubility parameter. See Ref. 14. b) 1-Naphthalenesulfonate. c) The values in the preliminary report were corrected here.

tetrafluoroborate, in contrast to the increasing effect of this solvent to the selectivity of organic anions. The hydrogen bonding ability of the solvents seems also to play an important role in the selectivity characteristics of the sulfonate electrode. Table 3 summarizes the solvent effect on the selectivities of the sulfonate electrode in the presence and absence of ptOP. In the table, the hydrogen bonding component δ_h of solubility parameters[14] is also listed. The interference of the inorganic anions such as perchlorate, tetrafluoroborate and others decreased with increasing δ_h. In the presence of ptOP, however, no remarkable effect of the solvents is observed. This shows that the selectivity is primarily determined by ptOP. The effect of ptOP in nitrobenzene was not so significant as that in the other solvents. This result is due to the relatively high dielectric constant of nitrobenzene. No effect of solvents on the selectivity of 1-naphthalenesulfonate and benzenesulfonate was observed. Namely, these organic sulfonates seem to interact with solvent or ptOP in the same way as the objective ion like *p*-toluenesulfonate. The interference of ions such as perchlorate and tetrafluoroborate which interact weakly with proton was decreased remarkably by the addition of ptOP. On the other hand, the interference of ions such as nitrite and chloride which strongly interact with proton did not always decrease but even increased in some cases.

Conclusion

From the above discussion, it is concluded that the phenol primarily governs the selectivity of the sulfonate electrode and the membrane solvent influences in a minor extent. For the optimum selection of phenol in order to obtain the high selectivity, the hydroxyl group of the phenol should be little hindered sterically, and the solubility of the phenol should be large in a membrane solvent and small in a aqueous sample solution.

In conclusion, it was found that the recommended ion-exchanger for *p*-toluenesulfonate was 0.05 M TOMA pTS with 0.5 M ptOP in *o*-dichlorobenzene. The potentiometric response characteristics of this ion-exchanger were as follows: (1) the linear response range is 10^{-1} M—$10^{-3.8}$ M, (2) the usable response range is 10^{-1} M—10^{-5} M, (3) the slope is 61 mV/decade, and (4) the response time at 10^{-2} M is within 3 min.

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