Synthesis and Exchange Properties of Sulfonated Poly(phenylene sulfide) with Alkali Metal Ions in Organic Solvents

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Sulfonated poly(phenylene sulfide) (SPPS) polymers were prepared by sulfonation of poly[methyl[4-(phenylthio)phenyl]sulfonium trifluoromethanesulfonate] (PPST) with fumic sulfonic acid (10% SO_3-H_2SO_4) and demethylation with aqueous NaOH solution. The equilibrium constants of ion exchange reactions between alkali metal cations (Li^+, Na^+, and K^+) and SPPS ion exchanger in organic solvents such as tetrahydrofuran (THF) and dioxane were measured. The equilibrium constants of ion exchange reactions increased as the polarity of the solvent increased, and the reaction temperature decreased. The equilibrium constants of the ion exchange reaction (K_{eq}) also increased in the order of Li^+, Na^+, and K^+. To elucidate the spontaneity of the exchange reaction in organic solvents, the enthalpy, entropy, and Gibbs free energy were calculated. The enthalpy of reaction ranged from -0.88 to -1.33 kcal/mol, entropy ranged from 1.42 to 4.41 cal/Kmol, and Gibbs free energy ranged from -1.03 to -2.55 kcal/mol. Therefore, the exchange reactions were spontaneous because the Gibbs free energies were negative. The SPPS ion exchanger and alkali metal ion bounding each other produced good ion exchange capability in organic solvents.

Keywords: Sulfonated poly(phenylene sulfide), Thermostable ion exchanger, Equilibrium constants of ion exchange in organic solvents.

Introduction

Recent rapid developments in industry have brought attention to the removal of toxic heavy metal ion from sewage, industrial, and mining wastewater. The removal of toxic heavy metal ions requires materials for the treatment of wastewater, such as ion exchanger.

In earlier experiments, the polymers for the cation exchange were prepared by the condensation of phenol-formaldehyde followed by the introduction of acidic groups such as sulfonic and carboxylic acid.[1] These polymers were less stable chemically and physically and relatively less moldable into shape of regular spheres.

At present, most strong acid cation exchange resins are based on sulfonated crosslinked polystyrene. The well-defined geometric shape of bead polymers can be obtained by the technique known as “suspension” or “bead” polymerization of styrene in the presence of a small amount of a crosslinking agent such as divinylbenzene.[2-6] The resulting polymers are chemically stable, but they have limited use at temperatures below 150 °C.

Many homopolymers, random copolymers, and block and graft copolymers containing aromatic rings or double bonds can be sulfonated. To qualify as appropriate materials for ion exchange resins, polymer materials must possess a number of properties such as excellent chemical and environmental resistance and especially high thermal and dimensional stability. Several attempts have been made in order to synthesize a more thermally stable cation exchange polymer containing a phenylene unit in the main chain. The route widely employed in the synthesis of sulfonated aromatic polymers is represented by the polymer reaction with fumic sulfonic acid, chlorosulfonic acid or sulfur trioxide-triethylphosphate complex.[7-10] Sulfonated poly(2,6-dimethylphenylene oxide) was categorized as available for use as an ion exchange resin.[11-15] Noshay and Robenson prepared sulfonated polysulfone and investigated its structure, thermal behavior, and mechanical properties in detail.[16] Also sulfonated poly(arylene ether sulfone) membranes have been useful in desalination application.[7-10] Nolte and co-workers reported the evaluation of poly(arylene ether ether sulfone)-based solid polymer electrolytes prepared by sulfonation of commercially available poly(arylene ether ether sulfone).[17] Sulfonated polycarbonates, polyesters, and polyimides are also mentioned in the literature.[18-20]

Poly(aryl sulfone) resins are important engineering thermoplastics that exhibit the concurrent properties of excellent resistance to hydrolysis and oxidation, excellent mechanical properties, good thermal stability, and toughness. Poly(phenylene sulfide) (PPS) has been known to have excellent thermal and chemical properties.[21-24] Therefore, PPS could be used as the polymer material of an ion exchanger.

In our laboratory, we prepared and studied many kinds of strong acid cation exchange resins containing the sulfonic acid group. We reported the ion exchange resins based on aromatic polymers such as poly(p-phenylene sulfide)[25] and poly(ether ether sulfone).[26] The sulfonated poly(phenylene sulfide) (SPPS) used in the present study was prepared by

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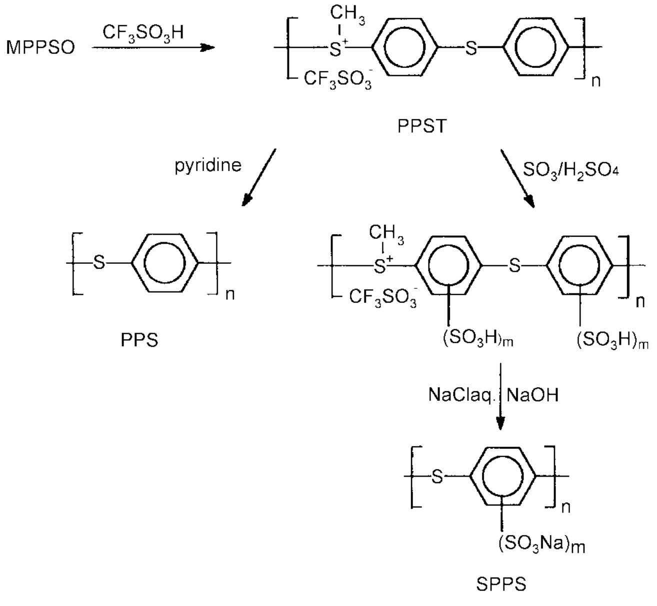
oxidative polymerization *via* poly(sulfonium cation) obtained from phenyl sulfoxide. We determined the spontaneity of the ion exchange reaction of sulfonated PPS from the equilibrium constants of ion exchange reaction for the alkali metal cations (Li, Na, and K) in THF and dioxane by using an UV-spectrophotometer.

Experimental Section

Materials. Thioanisole, bromine, trifluoromethanesulfonic acid, and methanesulfonic acid were purchased from Aldrich Co. and used without further purification. Potassium hydrogen carbonate (Kanto Co.) and methylene chloride (Junsei Chemical Co.) were used as received. Reagent-grade Li_2CO_3, Na_2CO_3, and K_2CO_3 were purchased from Jusnei Chemical Co. and were used as received. Picric acid was purchased from BDH Ltd. Tetrachloroethane, THF, dioxane, ethanol, and other chemicals were reagent grade and used without further purification.

Synthesis of Poly(phenylene sulfide) and Sulfonated Poly(phenylene sulfide). The soluble poly[methyl[4-(phenylthio)phenyl]sulfonium trifluoromethanesulfonate] (PPST) in organic solvents was synthesized by self-condensation polymerization of methyl(phenylthio) phenyl sulfoxide (MPPSO).[27,28] Poly(phenylene sulfide) (PPS) and sulfonated poly(phenylene sulfide) (SPPS) were prepared from PPST as shown in Scheme 1.

1) Poly(phenylene sulfide): A three-neck flask (250 mL) equipped with a Teflon-covered magnetic stirring bar, reflux condenser, thermometer, and N_2 gas inlet was charged with PPST (3 g, 7.8 mmol) and pyridine (30 mL). The reaction mixture was stirred at room temperature, becoming slightly pale yellow. After a few minutes, the color of the mixture turned into white. The reaction was continued for 1 h at room temperature, and the temperature of the mixture increased slowly to reflux. After refluxing for 20 h, the reaction was stopped by cooling the solution to room temperature. The solution was then poured into 10% HCl methanol solution (600 mL). The precipitate was washed with methanol and chloroform. The precipitate was purified by continuous extraction using a Soxhlet apparatus with ethanol for 24 h and dried in a vacuum oven at 50 °C for 48 h.



Scheme 1. Synthesis of sulfonated poly(phenylene sulfide).

2) Sulfonated Poly(phenylene sulfide): A three-neck flask (100 mL) equipped with a Teflon-covered magnetic stirring bar, reflux condenser, thermometer and N_2 gas inlet was charged with PPST (3 g, 7.8 mmol) and fumic sulfonic acid (30 mL 10% SO_3-H_2SO_4). The reaction proceeded for 12 h at 80 °C, then it was stopped by cooling the solution to room temperature, and the solution was poured into ethanol (300 mL). After the precipitate was washed with distilled water, it was redissolved in an aqueous NaCl/NaOH (0.5 M/ 0.1 M) solution (500 mL), which was refluxed for 10 h. The solution was poured into ethanol, and the obtained precipitate was washed with distilled water and ethanol. The polymer was purified by continuous extraction in a Soxhlet apparatus with ethanol for 24 h and dried in a vacuum oven at 40 °C for 24 h.

Ion Exchange Capacity in Non-Aqueous Solution. SPPS (1 g) was placed in an Erlenmeyer flask (250 mL) containing exactly 200 mL of 0.1 N Na-picrate solution in water and organic solvents (dioxane and THF), and it was allowed to stand for 24 h. The quantitative analysis of each metal element in the solution was conducted using Smith Hieftje for atom adsorption analyzer (Thermo Jarrau Ash Co., U.S.A). The ion exchange capacity was obtained by the following equation.

$$\text{Capacity (meq/g)} = \frac{(C_{st} - C_{eq}) \times V_{soln}}{22.989 \times M_p},$$

where C_{st} and C_{eq} are the concentration of metal ions in standard solution and equilibrium, respectively. M_p is the weight of the ion exchange resin, and V_{soln} is the volume of the whole solution.

Selective Adsorption Ability. To determine the selective adsorption ability of metal ions, 0.1 g of SPPS was added to 100 mL of a mixed metal aqueous solution and allowed to stand for 24 h. Then the SPPS was filtered, washed three times with distilled water, and dried in a vacuum oven at 60 °C.

The analyses of the relative adsorption amounts of metal ions were carried out in an EDAX (Energy Dispersive Analytical X-Ray).

Preparation of Alkali Picrate. The ethanol solutions of alkali metal salts (Li_2CO_3, Na_2CO_3, and K_2CO_3) were poured into the ethanol solution of picric acid. The crude picrate salts were filtered, recrystallized, filtered, and dried in a vacuum oven for 24 h and placed in a refrigerator at 4 °C.

Equilibrium Constant of Ion Exchange Reaction. A 10 mg sample of SPPS was placed in 20 mL stock solutions of Li, Na, and K picrates, respectively, and the solutions were agitated for 48 h. The concentrations of picrate salts were measured with an UV-spectrophotometer. The λ_{max}'s of Li, Na, and K picrates were 333 nm, 351 nm, and 357 nm in

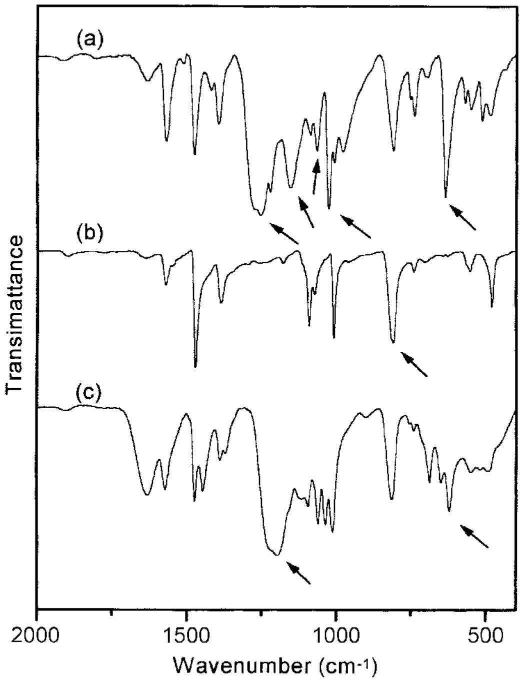


Figure 1. FT-IR spectra of (a) PPST, (b) PPS and (c) SPPS.

THF, and 335 nm, 347 nm, and 349 nm in dioxane, respectively. For 30, 40, 50, 60, 70, 80, and 90 mL stock solutions, the same procedure was followed by dilution.

Results and Discussion

The Fourier transform infrared spectra of PPST, PPS and SPPS are shown in Figure 1. The spectrum of PPST displays the characteristic absorption bands of PPS at 1565, 1471 and 1379 cm^{-1}, which are attributed to the ring stretching vibrations. The typical absorption band attributed to a C-H out-of-plane vibration of the 1,4-phenylene structure is observed at 810 cm^{-1}. The appearance of the C-F absorption bands at 1254, 1027 and 637 cm^{-1} and S=O absorption bands at 1155 and 1067 cm^{-1} indicate that the resulting polymer contained $CF_3SO_3^-$. These spectroscopic data reveal the formation of poly[methyl[4-(phenylthio)phenyl]sulfonium trifluoromethanesulfonate] (PPST) (Figure 1a).[27]

To convert from PPST to PPS, the demethylation was carried out using pyridine as a nucleophile. The IR spectrum of the resulting polymer is shown in Figure 1b. The absorption bands attributed to the $CF_3SO_3^-$ disappeared in PPST. The resulting polymer also shows a band attributed to a C-H out-of-plane vibration of the 1,4-phenylene structure at 810 cm^{-1}. This indicates the linear polymer with para substituted phenyl ring.[28]

SPPS was prepared by demethylation of sulfonated PPST. The IR spectrum of SPPS is shown in Figure 1c. The absorption bands attributed to the $CF_3SO_3^-$ disappeared in SPPS. The sulfonic acid groups were confirmed by the presence of the high absorption band of the SO_3H group at 1200 cm^{-1} and the S-O bond at 650 cm^{-1}. From these results we concluded that the sulfonation in poly(ethylene sulfide) was successfully performed.[28] It was found that the ion exchange capacity of SPPS was 4.11 meq/g, and the degree of sulfonation per repeating unit was 0.78 by a base line method of IR absorbance.[25]

Table 1. Na^+ Ion Exchange Capacity of SPPS in aqueous and organic solvent at room temperature

Solutions	Dioxane	THF	Water
Capacity (meq/g)	3.60	3.72	4.07

Table 2. Relative Adsorption of Metal Ions for SPPS ion exchanger in aqueous at room temperature

Elements	Total	Na(I)	K(I)	Mg(II)	Ba(II)
meq/g	4.01	0.47	0.54	1.27	1.74

Ion Exchange Capacity in a Non-Aqueous System. Generally, ion exchange ability of an ion exchanger can also be observed in a non-aqueous system, but the exchange rate is much slower than that in an aqueous solution, and the exchange capacities are dependent on the solvent. The ion exchange capacities of SPPS in organic solvents are listed in Table 1. As shown in Table 1, the ion exchange capacities in an organic solvent system are lower than those in an aqueous system, and they are related to dielectric constant of the organic solvent. The dielectric constants of dioxane, THF, and water are 2.2, 7.4, and 77.4, respectively, and the ion exchange capacity values in each organic solvent system are 3.60, 3.72, and 4.07 meq/g. As shown in Table 1, ion exchange capacity increases with increasing solvent polarity.

Selectivity of Metallic Ions. The ion exchange capacity increased with increasing the charge and atomic number of the ion in the same charge because of the electric attraction between exchange groups and ions. They followed the general order of exchange for dilute metal solutions but changed slightly at higher concentrations and higher temperatures of metal solution and by the pH of metal solution. Table 2 shows the relative amount of adsorbed metal ions in mixed metal solution analyzed by EDAX. The amount of adsorption ions increased with increasing atomic number. From these results, it was found that ions with two positive charges were adsorbed much more rapidly than ions with one positive charge, and the ions with the same valence ions were adsorbed easily as the atomic number increased.

Equilibrium Constant of Ion Exchange Reaction (K_{eq}). The equilibrium constants of ion exchange reaction (K_{eq}) between metal ions and the SPPS ion exchanger were obtained with the following procedure. It was supposed that the SPPS ion exchanger and metal picrate reacted as in the following equation.[29]

$$P - SO_3H + M^{n+}nPi^- \rightleftarrows (P - SO_3^-)_nM^{n+} + n \cdot \text{Picric Acid}, \qquad (1)$$

where $P - SO_3H$ and $(P - SO_3^-)_nM^{n+}$, respectively, represent the free SPPS ion exchanger and SPPS ion exchanger bonded with metal picrate. $M^{n+}nPi^-$ is unbinding picrate in the solution, the concentration of which was measured by

UV spectrophotometer. The concentrations of all these SPPS ion exchangers in Eq. (1) were equal to $[P - SO_3H]_{total}$, and the number of SPPS ion exchangers attached to metal ions was proportional to *n*. Substituting these conditions into eqn (1) produced Eq. (2). The concentration of the resin bound by metal ions can be calculated from Eq. (3).

$$[P - SO_3H]_{total} = [P - SO_3H]_{free} + [(P - SO_3^-)_nM^{n+}] \cdot n \quad (2)$$

$$[(P - SO_3^-)_nM^{n+}] = [M^{n+}nPi^-]_{total} - [M^{n+}nPi^-]_{free} \quad (3)$$

The equilibrium constants of the ion exchange reaction for picrate salt of SPPS ion exchanger were calculated by following the Klotz equation obtained from Eqs. (1), (2), and (3), where $[(P - SO_3^-)_nM^{n+}]$ represents the concentration of SPPS ion exchanger bonded with metal picrate.

$$\frac{1}{r} = \frac{[P - SO_3H]_{total}}{[(P - SO_3^-)_nM^{n+}]} = \frac{[P - SO_3H] + n[(P - SO_3^-)_nM^{n+}]}{[(P - SO_3^-)_nM^{n+}]}$$

$$= \frac{[P - SO_3H]_{free}}{[(P - SO_3^-)_nM^{n+}]} + n \quad (4)$$

$$K_{eq} = \frac{[(P - SO_3^-)_nM^{n+}] \cdot [\text{Picric Acid}]^n}{[P - SO_3H]_{free} \cdot [M^{n+}nPi^-]} \quad (5)$$

$$\frac{1}{r} = \frac{[P - SO_3H]_{free} \cdot [\text{Picric Acid}]^n}{K_{eq} \cdot [P - SO_3H]_{free} \cdot [M^{n+}nPi^-]_{free}} + n \quad (6)$$

If *n* was equal to unity, the concentration of picric acid was equal to the concentration of binding alkali metal ion from Eq. (1).

$$\frac{1}{r} = \frac{[(P - SO_3^-)_nM^{n+}]}{K_{eq} \cdot [M^+Pi^-]_{free}} + 1, \quad (7)$$

where $1/r$ was $[P - SO_3H]_{total}/[(P - SO_3^-)_nM^{n+}]$.

From the plot of $1/r$ versus $[(P - SO_3^-)_nM^{n+}]/[M^+Pi^-]_{free}$, K_{eq} was obtained from the slope and the bonding number of binding SPPS ion exchanger ($1/n = 1/1$) was determined from the intercept, where $[M^+Pi^-]_{free}$ represented unbinding picrate. Figures 2, 3, and 4 show the plots of $1/r$ versus $[(P - SO_3^-)_nM^{n+}]/[M^+Pi^-]_{free}$ of alkali metal ions for SPPS ion exchanger within the range from 10 °C to 40 °C in THF and dioxane.

As the dielectric constant (ε) and the polarity of a solvent increased, the reaction constant of ion exchange increased. As shown in Figures 2, 3, and 4, the equilibrium constant of ion exchange reaction (K_{eq}) in THF ($\varepsilon = 7.4$) was larger than that in dioxane ($\varepsilon = 2.2$). With decreasing reaction temperature, the K_{eq} value for alkali metal ions increased. The calculated K_{eq} values were presented in Table 3. The equilibrium constants of ion exchange reaction (K_{eq}) were calculated from the slopes of the lines in Figures 2, 3, and 4. The equilibrium constants of ion exchange reaction (K_{eq}) increased in the order of Li^+, Na^+, and K^+.

The K_{eq} values were plotted in Figure 5 by means of Van't Hoff method. Gibbs free energy (ΔG) was equal to the $-RT \ln K_{eq}$ in reactive solution. ΔG was dependent on the temperature.

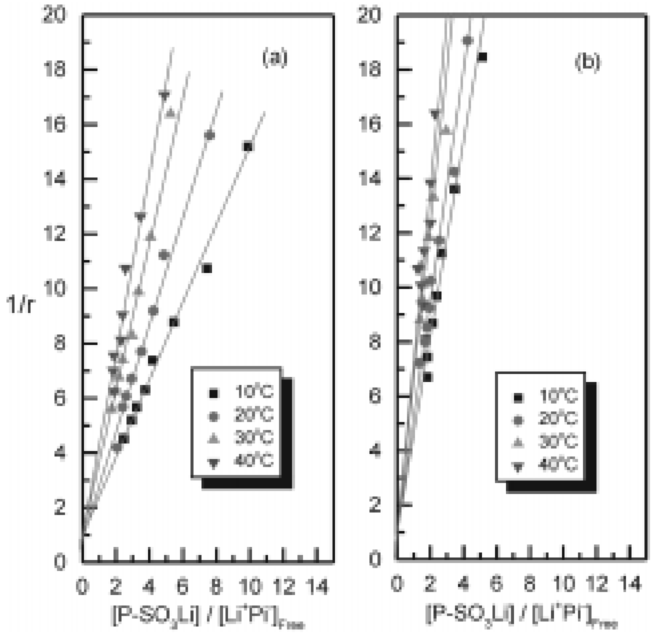


Figure 2. Binding of Li-picrate to SPPS in (a) THF and (b) dioxane.

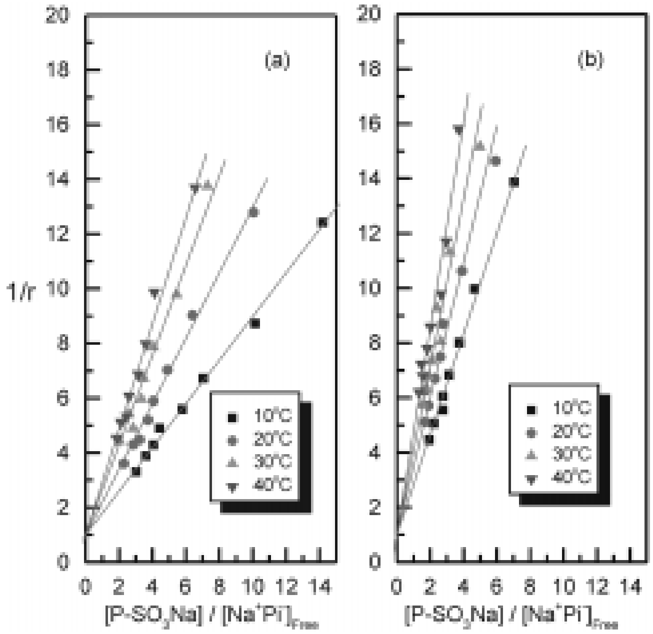


Figure 3. Binding of Na-picrate to SPPS in (a) THF and (b) dioxane.

$$\frac{d(\Delta G/RT)}{dT} = -\frac{\Delta H}{RT^2} \quad (8)$$

$$-\frac{d\ln K_{eq}}{dT} = -\frac{\Delta H}{RT^2} \quad (9)$$

$$\ln K_{eq} = -\frac{\Delta H}{RT} + C \quad (10)$$

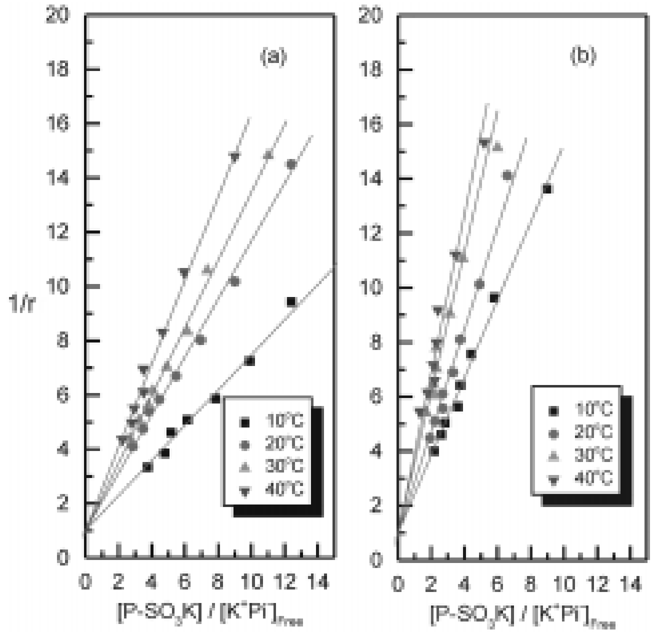


Figure 4. Binding of K-picrate to SPPS in (a) THF and (b) dioxane.

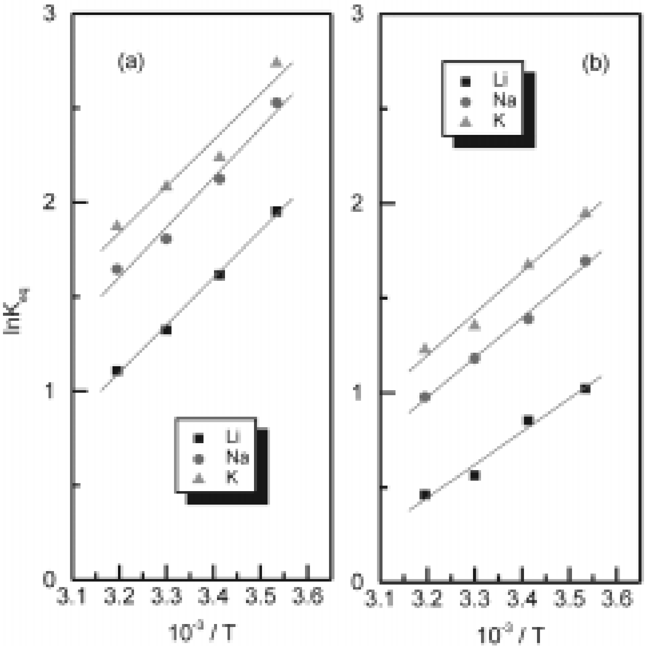


Figure 5. In K_{eq} *vs*. T^{-1} plots for reaction of SPPS with alkali metal picrate in (a) THF and (b) dioxane.

Table 3. K_{eq} of Alkali Metal Picrates for SPPS Ion Exchanger in THF and Dioxane

Temp. (°C)	K_{eq}					
	Li		Na		K	
	THF	Dioxane	THF	Dioxane	THF	Dioxane
10	7.05	2.78	12.53	5.45	15.44	7.01
20	5.03	2.35	8.36	4.02	9.37	5.35
30	3.76	1.76	6.09	3.27	8.02	3.87
40	3.03	1.59	5.19	2.66	6.50	3.42

Enthalpy (ΔH) was calculated from the slopes of the plots in Figure 5, where the enthalpy of exchange reaction showed a negative value. Entropy was obtained from $\Delta S = \Delta H/T + R \ln K_{eq}$, which showed a positive value (Table 4). ΔH value was in the range from -0.88 to -1.33 kcal/mol, which implied that the exchange reaction between the SPPS ion exchanger and alkali picrate was exothermic. Similarly, it was found that the ΔS value was in the range from 1.42 to 4.41 cal/Kmol. From ΔH and ΔS, Gibbs free energy (ΔG) values were obtained, ranging from -1.03 to -2.55 kcal/mol. It was found that the ion exchange reaction of SPPS for alkali metals in organic solvent was spontaneous reaction due to the negative value of Gibbs free energy. From these results, it was concluded that the stability of system increased when SPPS ion exchanger and alkali metal ions bound each other. Therefore, the newly manufactured SPPS ion exchanger showed good ion exchange capability for alkali metal ions in organic solvents.

Conclusion

Sulfonated poly(phenylene sulfide) (SPPS) was prepared from poly[methyl[4-(phenylthio)phenyl]sulfonium trifluoromethanesulfonate] (PPST). The reaction constants of ion exchange between SPPS as an ion exchange resin and alkali metal cation (Li, Na, K) dissolved in THF and dioxane were determined. The sulfonation of PPS was confirmed by the presence of the high absorption band of the SO_3H group at 1200 cm^{-1} and the S-O bond at 650 cm^{-1}. As the polarity of the solvent increased and the reaction temperature decreased, the equilibrium constant of ion exchange reaction became larger. The equilibrium constants of ion exchange reaction increased in the order of Li^+, Na^+, and K^+.

ΔH values ranged from -0.88 to -1.33 kcal/mol, and ΔS values ranged from 1.42 to 4.41 cal/K·mol. From the ΔH and ΔS, Gibbs free energies (ΔG) were obtained and ranged from -1.03 to -2.55 kcal/mol. It was found that the ion exchange

Table 4. In K_{eq}, Enthalpy, Entropy, and Gibbs Free Energy Changes on the binding of SPPS Ion Exchanger with Alkali Metals in THF and Dioxane

Alkali Metals	In K_{eq} (at 25 °C)		-ΔH (kcal/mol)		ΔS (cal/K · mol at 25 °C)		-ΔG (kcal/mol at 25 °C)	
	THF	Dioxane	THF	Dioxane	THF	Dioxane	THF	Dioxane
Li	1.49	0.78	1.26	0.88	2.95	1.42	2.14	1.30
Na	2.01	1.30	1.33	1.06	4.00	2.58	2.52	1.83
K	2.22	1.54	1.23	1.11	4.41	3.06	2.55	2.02

reactions of SPPS for alkali metal ions in organic solvent were spontaneous reactions, as indicated by negative Gibbs free energies. When SPPS ion exchanger and alkali metal ions bound each other, it had good ion exchange capability in organic solvent.

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