

Study of the Ion Exchange Properties of Colloidal Particle Consisting of Polyaniline and Poly(vinylalcohol)

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Colloidal particles consisting of polyaniline, poly(vinylalcohol) and silica gel powder were prepared and their ion exchange properties were investigated. The colloidal particles can incorporate anions from the acidic solution, because of the protonation of polyaniline. Further, incorporated anions are exchangeable with other anions in the immersed solution and also released in the basic solution by the deprotonation. The ion exchange properties of this colloid can be evaluated by use of the ion exchange equilibrium constants and ion exchange capacities. The former follows the hydrophobic interaction between anions and colloid, and its sequence was similar to the Hofmeister series. The latter was resulted from the size effects between the exchangeable anion sizes and the pore sizes in the colloidal particle. The micropore in the colloid was formed by the dopant anion in the polymerization. Then, the pore sizes in the colloid were varied by the polymerized condition, such as the concentration ratio of PVA/PANI and species of the containing dopant anion.

Key Words: Ion exchange, Polyaniline, Colloid, Poly(vinylalcohol),

1. INTRODUCTION

Polyaniline (PANI) is composed of structural repeating unit formed by two aniline molecules. These units can be adopted in reduced (amine) state or in oxidized (imine) state. The degree of oxidation may vary smoothly between fully reduced leucoemeraldine form and completely oxidized pernigraniline.¹⁻³ All forms of PANI can be converted by chemical and electrochemical oxidation and reduction.^{4,5} In the acidic solution, both reduced and oxidative unit of PANI can be protonated. The nitrogen atom in PANI can protonate easily in strongly acidic media. Then anions in the solution are incorporated with protonation of PANI as dopant anion. It has been reported that a dopant anion can be exchanged for another anions in the immersed solution at equilibrium.⁶ In addition, dopant anion is released by the deprotonation in the neutral pHs.⁷ For these reasons, polyaniline is expected to use the functional ion separator. But the ion exchange capacity of PANI powder is not sufficiently.

To solve the problem of capacity, this study was performed using the composite colloidal particle consisted with PANI and poly(vinylalcohol) (PVA). Colloidal particle of PANI has been proposed for the improvement of poor processability. Polyaniline is insoluble in most solvent and decomposes below melting point when heated. PVA/PANI colloid has

been prepared by the copolymerization of aniline onto appropriate polymeric surfactant.⁸⁻¹¹ In this method, colloidal particle formed a relatively uniform spherical morphology with an average diameter of 150-220 nm and held a large surface area.

There have been various investigations of the ion exchange selectivity of the PANI.^{12,13} Polyaniline powder indicated different selectivity from commonly anion exchange resin. But the reason for its variation of selectivity is not fully understood. The purpose of this work is the evaluation of ion exchange properties of PANI and the elucidation of the difference between PANI colloidal powder and commonly ion exchange resin. The mechanism of ion exchange property in the colloidal particle should be useful for the development of designable ion exchange separator.

2. EXPERIMENTAL

2.1 Apparatus

The anions in the sample solution were determined by Hitachi ion chromatography composed of L-6000 pump, L-3720 conductivity detector and L-5020 column oven with sample injector. The separation column was Showdex IC I-524A (4.6mm I.D.×100mm, Showa Denko). The analytical signals were recorded and processed with a Hitachi D-2500 Chromato Integrator. Deionized-distilled water was prepared by AQUEOUS

GS-20 (Advantec).

2.2 Reagents and Chemicals

Poly(vinylalcohol) (PVA) was purchased from Ishizu Chemicals (DP=300), and silica gel powder purchased from Waco Chemicals (300 mesh). All the other chemicals used were reagent grade. All of the solutions containing various anion were prepared by dissolving sodium or potassium salts in deionized-distilled water.

2.3 Preparation of the PVA/PANI colloidal powder

The colloidal powder was prepared by adsorption on silica gel powder of the PVA/PANI composite colloidal particle. Colloidal particle incorporated with Cl^- (PVA/PANI(Cl^-)) was synthesized by the chemical method. One hundred milliliter mixture solution of 0.2 mol l^{-1} HCl dissolved with 0.03 mol aniline and 3.52 g PVA were stirred with silica gel powder (15 ml). To this mixture, 0.01 mol of ammonium peroxodisulfate was added with stirring. The stirring was continued for 12 hour at room temperature. The composite colloids fixed on silica gel powder was separated by decantation and washed with $1.0 \times 10^{-3} \text{ mol l}^{-1}$ HCl solution until the washings were no longer colored. This powder was kept in $1.0 \times 10^{-3} \text{ mol l}^{-1}$ HCl solution. PVA/PANI colloid powder incorporated with another dopant anion were also prepared and washed by same method in corresponding acid solution of same concentration.

2.4 Ion exchange procedure

PVA/PANI(Cl^-) was introduced into a 100 ml flask and several washings were made with $1.0 \times 10^{-3} \text{ mol l}^{-1}$ HCl solution. After that, 10 ml of sample solution was added. Sample solution which contained various concentration of sodium nitrate and was adjusted at pH4 with HNO_3 . In order to reach the equilibrium between colloid and the solution, the flask was shaken for 24 hours at room temperature. After that, the changes of concentrations of nitrate and chloride ions in the solution were measured using ion chromatography. Using the solution of another anion, the same experiments were also carried out.

3. RESULTS AND DISCUSSION

3.1 Determination of ion exchange properties.

The ion exchange properties of PVA/PANI colloid was studied by the following method which was similar to that reported by Kataoka *et al.*¹⁴ The following equation has been obtained at the ion exchange equilibrium of the ion exchange resin in the chloride form with other monovalent anion in the aqueous solution.



$$K_{\text{Cl}}^{\text{X}} = \frac{q_{\text{X}} C_{\text{Cl}}}{q_{\text{Cl}} C_{\text{X}}}$$

Where K_{Cl}^{X} is the ion exchange equilibrium constant, C and q are the concentrations in aqueous solution and resin respectively. Introducing the ion exchange capacity of resin, $Q (= q_{\text{X}} + q_{\text{Cl}})$, into this equation, following equation is obtained.

$$q_{\text{X}} = Q - \frac{1}{K_{\text{Cl}}^{\text{X}}} \frac{q_{\text{X}} C_{\text{Cl}}}{C_{\text{X}}}$$

This equation shows that plot of q_{X} against $(q_{\text{X}} C_{\text{Cl}})/C_{\text{X}}$ is a linear relationship with a slope of $-1/K_{\text{Cl}}^{\text{X}}$ and the intercept of this straight line is the ion exchange capacity of resin. The ion exchange constant, K_{Cl}^{X} and total ion exchange capacity, Q can be calculated in this method.

Two milliliters of PVA/PANI colloidal powder was introduced into a 100 ml flask and 10 ml of the sample solution containing anion with a concentration range of 1.0×10^{-3} to $1.0 \times 10^{-4} \text{ mol l}^{-1}$ was added. The flask was shaken for 24 hour at room temperature. After that, the concentration of exchangeable anion and exchanged dopant anion were determined by using of ion chromatography and q_{X} and $(q_{\text{X}} C_{\text{NO}_3})/C_{\text{X}}$ values were calculated.

3.2 Influence of exchangeable ion species

The ion exchange amounts of PVA/PANI (NO_3^-) and PVA/PANI(Cl^-) colloidal powders for various anions in the sample solutions were measured. The results are shown in Table I. The ion exchange amounts increase in the sequence of $\text{Br}^- < \text{Cl}^- < \text{NO}_3^- < \text{ClO}_4^- < \text{SCN}^-$. This sequence is similar to the Hofmeister series¹⁵ ($\text{Cl}^- < \text{Br}^- < \text{NO}_3^- < \text{SCN}^- < \text{ClO}_4^-$) which is known as the lipophilic order of the various anions. The ion exchange selectivity of this colloid mainly related to the lipophilic affinity between colloid

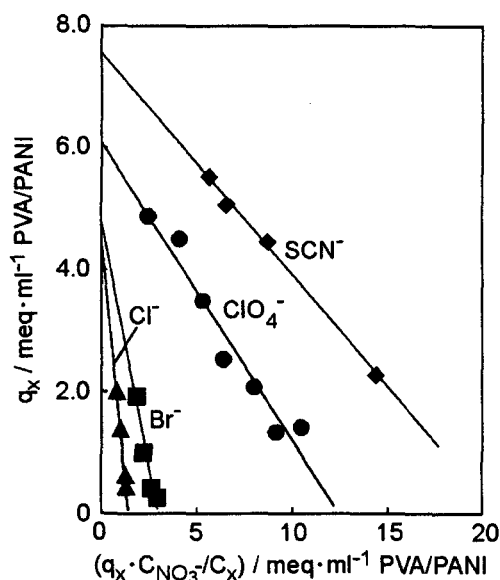
Table I Ion exchange amounts of the PVA/PANI colloidal powder for anions.

Solution ^{a)}	ion exchange amount / $\mu\text{mol ml}^{-1}$ PVA/PANI	
	PVA/PANI(Cl ⁻) ^{b)}	PVA/PANI(NO ₃ ⁻) ^{b)}
Cl ⁻	-	1.67
Br ⁻	1.62	1.56
NO ₃ ⁻	2.21	-
ClO ₄ ⁻	2.67	2.20
SCN ⁻	2.98	2.50

a) Solution; 1.0×10^{-3} mol dm⁻³ sodium salt, pH5b) PVA/PANI colloidal powder prepared with Cl⁻ or NO₃⁻

and exchangeable anion. But this ion exchange selectivity does not agree with the Hofmeister series simply, such as Cl⁻, ClO₄⁻ and SCN⁻.

The equilibrium plots for the ion exchange between PVA/PANI(NO₃⁻) colloidal powder and various anion in the solution are shown in Fig.1. The plot of q_x and $(q_x C_{\text{NO}_3})/C_x$ was a straight line and the intercept of each line corresponds to the ion exchange capacity. The sequence of the slope obtained each lines are fitted order of the Hofmeister series. But the lines obtained in ClO₄⁻ solution was likely parallel to the line obtained in SCN⁻. It means the ion exchange equilibrium constants, $K_{\text{NO}_3}^x$, were varied corresponding to the lipophilic affinity between colloid and exchangeable anion. In contrast, the intercepts of their lines are increased according to the ion exchange amounts. The ion exchange equilibrium constants and the ion exchange

Fig.1 Equilibrium plots for the ion exchange between PVA/PANI(NO₃⁻) and various anion ($x=\text{Cl}^-$, Br⁻, ClO₄⁻ and SCN⁻) in the solution adjusted at pH5.

capacities calculated from the ion exchange equilibrium plot are shown in Table II. The ion exchange capacities calculated from these plots were compared with the ion exchange amounts measured in the solution. The capacities are consistent with the sequence of the ion exchange amounts. It is consider that the disparity in the order of the ion exchange selectivity and lipophilicity are attributeable to the difference of the ion exchange capacities. But the ion exchange amount and property of chloride were not corresponding. This discrepancy is probably due to absorption other than ion exchange.

In addition, these order of ClO₄⁻ and SCN⁻ is different from lipophilic order. This difference can be explained by the size effects of the anion and the pore of the PVA/PANI colloidal matrix. That is to say, these sequence are influenced by the ion sizes in the colloidal matrix. Thus, thiocyanate can pass through colloidal matrix easier than perchlorate and exchange at the inner cationic site of PANI. This difference of ion sizes is attributed to the molecular structure. The linear structure of thiocyanate behaves smaller anion than the regular tetrahedron structure of perchlorate. It is suggested that the ion exchange of anion at inner exchangeable site is inhibited by the sieving effect due

Table II Ion exchange equilibrium constants and capacities of the PVA/PANI for anions.

Anions ^{a)}	PVA/PANI(Cl ⁻) ^{b)}		PVA/PANI(NO ₃ ⁻) ^{b)}	
	K	Q / meq ml ⁻¹	K	Q / meq ml ⁻¹
Cl ⁻	-	-	0.0317	4.53
Br ⁻	0.388	2.97	0.0622	4.86
NO ₃ ⁻	0.395	3.26	-	-
ClO ₄ ⁻	0.412	3.27	0.203	6.13
SCN ⁻	0.428	4.27	0.274	7.54

a) Solution containing various concentration of sodium salt, pH4

b) PVA/PANI colloidal powder prepared with Cl⁻ or NO₃⁻Table III Ion exchange equilibrium constants and capacities of the PVA/PANI prepared with various dopant for Br⁻.^{a)}

Dopant	PVA/PANI(Cl ⁻) ^{b)}		PVA/PANI(NO ₃ ⁻) ^{b)}	
	K	Q / meq ml ⁻¹	K	Q / meq ml ⁻¹
ClO ₄ ⁻	0.452	1.05	0.249	7.88
Cl ⁻	-	-	0.304	9.81
NO ₃ ⁻	0.510	2.46	-	-
BS ^{-c)}	0.585	3.86	0.383	12.2

a) Br⁻ solution added as sodium salt, pH4b) PVA/PANI prepared with various dopant anion and replaced to NO₃⁻ or Cl⁻.

c) BS; benzenesulfonic acid

to the pore of the colloidal matrix. The higher ion exchange capacity of SCN^- leads to the greater value of the ion exchange amounts. In addition, Cl^- , Br^- and NO_3^- were formed greater anions than ClO_4^- and SCN^- by the hydration. The water of hydration with ClO_4^- and SCN^- can be eliminated easily in the hydrophobic atmosphere such as composite matrix. Namely, the ion sizes in the colloid were related to the hydration energy, ionic radius and radius of a hydrated ion. The diffusion of ions into the polymer matrix are affected by the pore sizes formed by the incorporated anions in polymerization. The ion exchange capacity can be controlled by the colloidal matrix formed in the polymerization.

3.3 Influence of dopant anion species

The ion exchange property of the PVA/PANI colloidal powder polymerized with various dopant anion was investigated. The PVA/PANI colloidal powder was prepared by the same method in the solution containing dopant anion and washed by the equivalent acid solution. Then, they were immersed in the Cl^- or NO_3^- solution for replacing of dopant anion to them. After that, the ion exchange properties between these colloidal powder and Br^- in the solution at pH4 was measured. Table III shows the variation in the ion exchange equilibrium constants and ion exchange capacities of the dopant anion species in the polymerization.

These results showed that the ion exchange capacity was related to the coexisted anion in polymerization. This order of ion exchange capacity was similar to the sequence of capacity obtained from various exchangeable anions as described above. This observation means the larger dopant anions such as benzenesulfonic acid (BS^-) form large mesh colloidal matrix. Then, the exchangeable anions can pass through easily and exchange at the inner cationic site of PVA/PANI colloid. In contrast, $Q_{\text{ClO}_4^-}$ indicate small in this experiment. It was due to the closely colloidal matrix formed by the ClO_4^- . Therefore perchlorate anion adopts a bare form in the colloidal matrix because of its lower hydration energy. That is to say, the colloidal matrix can be controlled by the dopant anion sizes in the polymerization like molecular template. These colloidal matrix sizes are mainly based on a

radius of a hydrated ion, but hydrophobic ion behaves smaller ions because of the weakly hydration.

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