

# Ion Exchange Properties and Kinetic Behaviour of Polyaniline-coated Silica Gel for *p*-Toluenesulphonic Acid and Methanesulphonic Acid

S. Hossein Hosseini\* and Peyman Noor

Department of Chemistry, Faculty of Science, Imam Hossein University, Tehran, I.R. Iran

Received 7 November 2003; accepted 13 June 2004

## ABSTRACT

Polyaniline and polypyrrole are two conducting polymers that show ion-exchange properties. Due to their easy processibility, they can be used for surface modification of different substances. For instance they can be coated on silica particles. In this work anion-exchange properties of polyaniline-coated silica gel for some sulphonic acid anions such as, *p*-toluenesulphonic acid (PTSA) and methanesulphonic acid (MSA) were investigated qualitatively and quantitatively. Also the concentration effects of sulphonic acids and flow rates were investigated and kinetic experiments were performed. The column capacities for two acids were calculated and the accuracy of titrations with micropipet were confirmed with UV-Vis spectrophotometric experiments. Also the effect of ion exchange on conductivity of the polymer was investigated.

### Key Words:

polyaniline;  
polyaniline coating;  
ion exchange;  
silica gel;  
kinetics.

## INTRODUCTION

Polyaniline (PANi) is a conducting polymer with electrochemical activity that has been widely investigated in the past decade [1-2]. Several applications of the polymer have been proposed and demonstrated [3,4]. We used polypyrrole(PPy) and

PANi blends for detection of some toxic gases and vapours [5,6]. Whereas, most of the applications deal with the electrochemical activity and electronics, a few are concerned with its ion-exchange properties [7,8]. Because of the attractive

(\*) To whom correspondence should be addressed.  
E-mail: hhoseini@ihu.ac.ir

electrical, optical and chemical properties of PANi and (PPy), both polymers have recently been used in the surface modification of various substances. A particularly interesting example is the use of PANi modified glassy carbon particles as the stationary phase in ion-exchange chromatography [9]. It has often been observed that glass surfaces immersed in the aqueous reaction mixture used in the oxidation of aniline became coated with a thin PANi film [1]. The typical film thickness varied between 50 and 400 nm depending on the reaction conditions. The coating protocol can be applied to the surface modifications of microspheres of the same chemical nature, SiO<sub>2</sub> with PANi hydrochloride. The deposition of thin PANi and PPy coating onto monodisperse silica particles of 1 μm diameter was reported by Armes et al. [10]. Stejskal and co-worker [11] prepared PANi in the presence of silica having 7 μm diameter and 35 nm pore size. Electron microscopy showed that a solid film of PANi was produced on the surface of silica microspheres. PANi over-layer has been similarly produced on silica gel microspheres of 15 μm in size [12]. Also 60-125 μm porous silica gel was coated with PPy. The silica gel modified with conducting polymers was proposed to be used in chromatographic and ion-exchange separations [13]. Emeraldine salt (half oxidized PANi,  $y = 0.5$ ) is the most conductive form of PANi, which can be obtained by protonation of emeraldine base and oxidation of leucoemeraldine base as shown in Scheme I. Besides the emeraldine, leucoemeraldine (fully reduced PANi,  $y = 1$ ) and pernigraniline (fully oxidized form,  $y=0$ ); nigraniline (75% oxidized form,  $y=0.25$ ) have also been reported [14].

In this article we have investigated anion exchange properties of PANi coated silica gel for *p*-toluenesulphonic acid (PTSA) and methanesulphonic acid (MSA). The kinetic behaviour was also investigated and column capacity for each acid was calculated.

## EXPERIMENTAL

### Reagents and Instruments

The *p*-toluenesulphonic acid (Merck) was purified by precipitation from a saturated solution at 0°C by introducing HCl gas. Then it was dried in vacuum desiccator over solid KOH and CaCl<sub>2</sub>. Methanesulphonic acid (Merck) was dried by azeotropic removal of water with

benzene then distilled under vacuum and fractionally crystallized by partial freezing. Acetone (Merck) was dried with anhydrous type 4A<sup>o</sup>, 1/8-inch bead (4-8 mesh) molecular sieves, and then it was distilled. Other reagents and materials were used in as received. Silica gel 60 (0.063-0.200 mm, Merck, SiO<sub>2</sub>,  $M=60.09$  g/mol, for column chromatography grade) was used.

UV-Visible spectra were obtained from filmed tin oxide glass electrodes by Perkin Elmer Lambda 15 spectrophotometer and electrical conductivities were measured by four-point probe device (home-made).

### Synthesis of PANi

30 mL Conc. HCl, 44 mL acetone and 176 mL distilled water were mixed together so a 250 mL solution was obtained. An amount of 180 mL of the solution and 10 mL of aniline were added into a 500 mL flask (covered with ice cubes-salt mixtures to maintain low polymerization temperature) equipped with an electromagnetic stirrer. Ammonium peroxydisulphate, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, of 22.8 g was dissolved into the remaining 70 mL of the solution. This mixture was then added into the reactor drop by drop for 1 h. The polymerization temperature 0-5°C was maintained for 5 h to complete the reaction. Then the precipitate obtained was filtered using G<sub>2</sub> sintered glass filter. The product was washed successively by distilled water (250 mL), methanol (150 mL), respectively, until the wash solution turned colourless. Then it was re-filtered and washed once again successively by one mole of distilled water, acetone, diethyl ether and 250 mL of NH<sub>4</sub>OH, thoroughly to obtain the emeraldine base form of polyaniline, and then it was dried at 60°C for 24 h. Finally a powder of insulating polyaniline(EB) polymer was obtained.

### Coating of Silica Gel by PANi

The obtained polymer (0.5 g) was dissolved in 20 mL formic acid. Then 5 g of silica gel powder (50-80 mesh) was added to the above solution and stirred for 30 min. Then the solvent was evaporated by keeping it in an oven. Finally a well coated silica particles were obtained.

### Packing the Column for Ion-exchange

The silica gel coated PANi particles were undoped by 50 mL NaOH 1 M and redoped with Cl<sup>-</sup> ion by immersing into 100 mL HCl 1M solution. Then it was filtered and washed to remove the excess acid and Cl<sup>-</sup> anion. It

is notable that due to the release of trace amounts of doped  $\text{Cl}^-$  anion when the polymer is washed with water, all washings and ion-exchange experiments were done in acetone. After drying the particles (2g), of PANi coated with silica gel was packed in column of 1 cm diameter and washed with acetone again. The received acetone from the column was tested for the existence of  $\text{Cl}^-$  anion by  $\text{AgNO}_3$  0.05 M solution until it was confirmed that there was no  $\text{Cl}^-$  anion in the solvent.

### Ion-exchange Experiments

After preparing the column, PTSA and MSA solutions with various concentrations were passed through the column at constant flow rate. The doped  $\text{Cl}^-$  anion in the polymer is exchanged by *p*-toluenesulphonate anion and  $\text{Cl}^-$  anion is released. The amount of Cl released due to anion-exchange was determined by the Volhard's back titration method with a micropipette. It is notable that the column was washed with 25 mL of pure acetone after the passage of each acid solution to ensure the exit of all released  $\text{Cl}^-$  anion. Also the column was regenerated by 1 M HCl and washed with acetone again before allowing the next acid solution to pass through the column. The experiments for MSA were performed in the same concentrations and flow rates as for PTSA.

## RESULTS AND DISCUSSION

### Ion-exchange Data

The result of ion exchange experiments for PTSA and

MSA is shown in Tables 1 and 2, respectively. As it is seen, the ion-exchange of sulphonic acid anions with the  $\text{Cl}^-$  anion of the polymer is quantitative up to 0.005 M concentration of acids and so the exchange percentage is 100%. These experiments were done in different flow rates of acids which show that the flow rate even at high flow rates (~4.5 mL/min) has no effect on ion-exchange property in 0.05M concentration of acids. This shows that the rate of ion-exchange behaviour is very high.

As it is noticed with the results of Table 1 both anions were able to exchange the  $\text{Cl}^-$  of the polymer quantitatively. This shows that the rate of ion exchange in both anions is high enough that the structural differences did not notably affect the results in concentrations tested.

### Spectrophotometric Determination

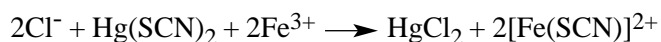
Some solutions of PTSA and MSA in these experiments were prepared and passed through the column in the same conditions as before but the  $\text{Cl}^-$  released was determined by spectrophotometric method and UV-Vis equipment. The results were compared with those determined by titration method and so confirmed the correctness of the results of titration method. For determination of  $[\text{Cl}^-]$  by spectrophotometric method, first several standard solutions of 10, 20, 30, 40 and 50 ppm of  $\text{Cl}^-$  in acetone were prepared. Then 2 mL of distilled water, 0.4 mL of ferric ammonium sulphate  $[(\text{SO}_4)_3\text{Fe}_2(\text{NH}_4)_2(\text{SO}_4).2\text{H}_2\text{O}]$  solution in nitric acid 9 M, 0.4 mL of saturated solution of mercury(II) thiocyanate,  $\text{Hg}(\text{SCN})_2$  in ethanol was added to each sample.

**Table 1.** The results of concentrations and flow rates of PTSA or MSA on anion-exchange.

[PTSA] or [MSA] M	V (mL)	PTSA or MSA entered the column (mmol)	Flow rate (mL/min) (±0.05)	Released $\text{Cl}^-$ (mmol) (±0.001)	Exchange percentage (%)
0.0025	5	0.0125	0.5	0.0125	100
0.005	5	0.025	0.5	0.025	100
0.01	5	0.05	0.5	0.045	90
0.02	5	0.1	0.5	0.076	76
0.005	5	0.025	1	0.025	100
0.005	5	0.025	2.28	0.025	100
0.005	5	0.025	4.6	0.025	100

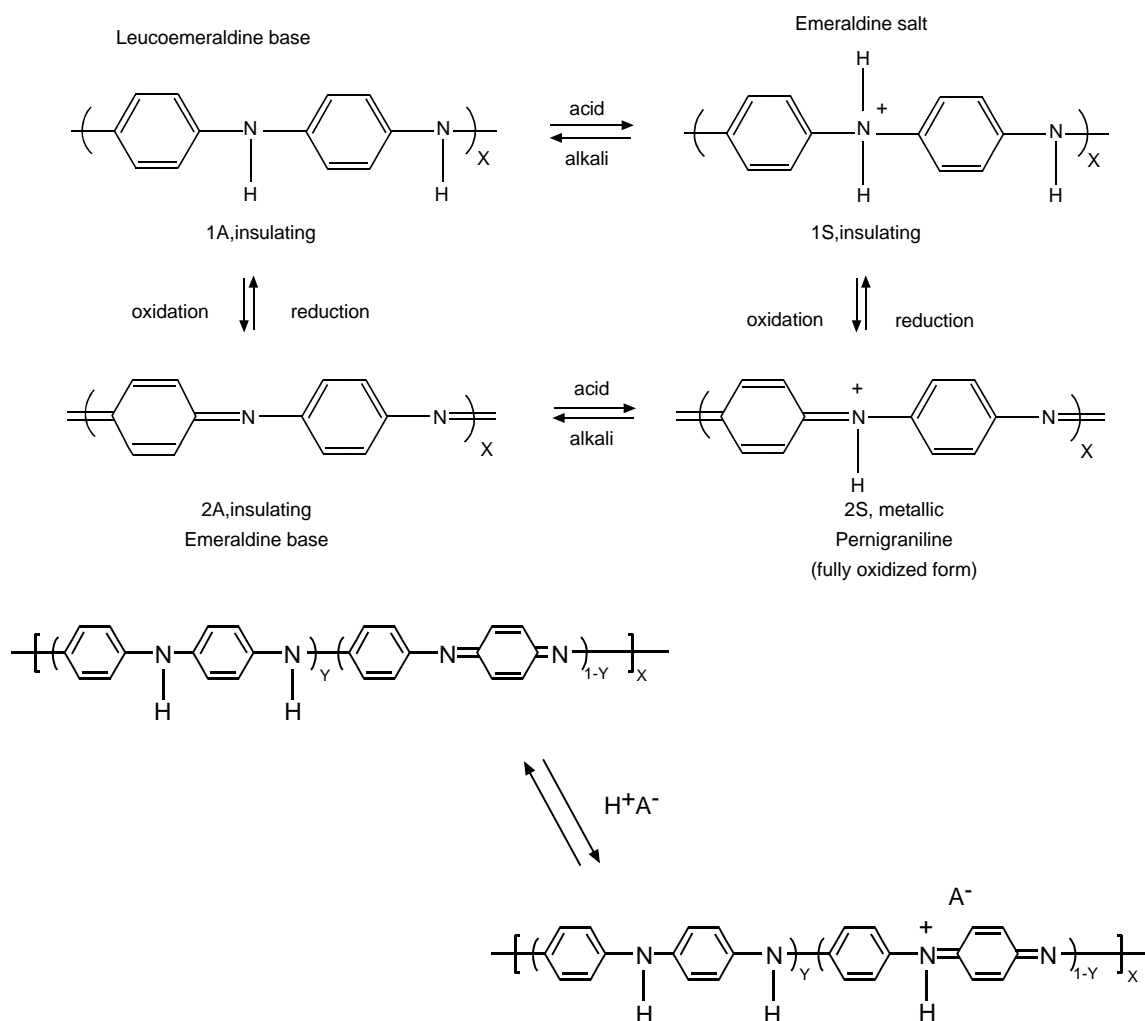
Absorbance value of solutions were recorded in 460 nm after 10 min. The calibration curve which shows good linearity is shown in Figure 1. This method is a very sensitive method for determination of  $[Cl^-]$  by its concentration in the 0.5-100 ppm range. After preparing the calibration curve the solutions in Table 3 were passed through the column and the  $Cl^-$  released was determined by this method. The results were compared with the results of the titration method as shown in Table 3. As it is seen the results of this method are in agreement with the results of the titration method and so confirm those results.

The basis of this method is on interchange of  $SCN^-$  ion by  $Cl^-$  ion. This will produce a colourful  $[Fe(SCN)]^{2+}$  complex in the presence of  $Fe^{3+}$  ion. The intensity of the colour depends on the Cl concentration.



### Kinetic Measurements

In these experiments kinetic and the rates of exchange for PTSA and MSA anions were investigated. First, the column was doped with HCl 1 M for about 1 h and then it was washed with pure acetone to remove the excess  $Cl^-$  as described before, and now the column was ready. Then 100 mL of PTSA solution (0.01 M) was poured into a separatory funnel and placed over the column using clamps. The valves of the separatory funnel and the column were adjusted so that the flow rate of the column remained constant. The leaving solution was collected 5 mL by 5 mL in separate test tubes and the amount of  $Cl^-$  released due to ion exchange was determined by the Volhard's back titration method in each



Scheme I. Structure of different forms of polyaniline.

**Table 2.** Comparison between titration and spectrophotometric results for MSA.

Acid	Acid conc.	Flow rate (mmol)	Absorbance [Cl <sup>-</sup> ]	Calibration curve [Cl <sup>-</sup> ]	Titration method [Cl <sup>-</sup> ]
MSA	0.005	2.29	0.594	0.025	0.025
MSA	0.005	1	0.629	0.026	0.025

**Table 3.** Electrical conductivity of silica gel coated by PANi before and after anion exchange.

Conductivity (S/cm) silica gel coated by PANi	Conductivity (S/cm) before anion exchange (Cl <sup>-</sup> doped)	Conductivity (S/cm) after anion exchange by PTSA	Conductivity (S/cm) after anion exchange by MSA
$2.1 \times 10^{-6}$	$3.6 \times 10^{-3}$	$7.4 \times 10^{-2}$	$1.2 \times 10^{-2}$

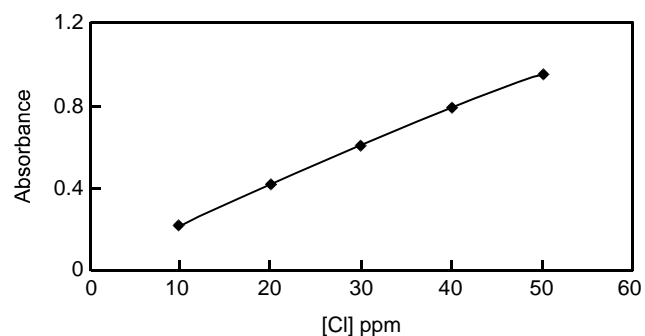
sample. In order to determine the flow rate of column more precisely, the flow rate in each sampling was calculated and the average was reported as the flow rate of column. We applied the same conditions of kinetic experiments for MSA. After the determination of [Cl<sup>-</sup>] in each sample the graph of [Cl<sup>-</sup>] versus acids (PTSA and MSA) passed (mL) through the column are plotted (Figure 2).

From the kinetic diagrams (Figures 2 and 3) it is obvious that both acids show very fast ion-exchange process so that more than 60% of the Cl content of the polymer is released during the leaving of the first 25 mL of each acid. Then as the Cl content of the polymer decreased the release of Cl<sup>-</sup> anion was also decreased and so the slope of the curve reduced until the Cl content of the polymer reached about 0.001 mmol. In this case it can be said that all exchangeable Cl<sup>-</sup> anions of the polymer have been released. So the total exchangeable Cl<sup>-</sup> ions of the polymer can be calculated. It is notable that the first 5 mL leaving the column has no Cl<sup>-</sup> ion, because it is a pure acetone in the

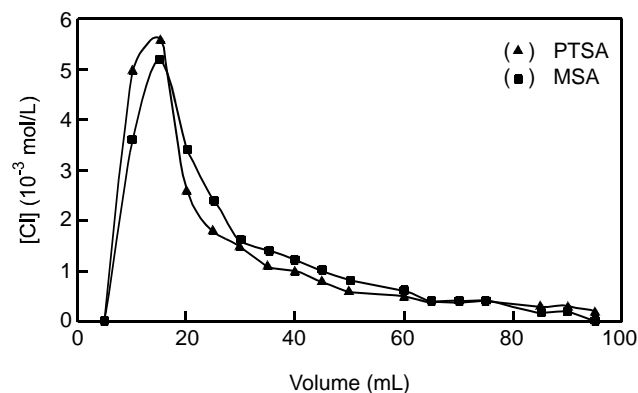
column and can be regarded as the retention volume of the column. As it is seen from the kinetic diagrams (Figures 2 and 3), the curve of PTSA anion shows a sharper peak than the curve of MSA anion. This little difference shows that the rate of ion-exchange for PTSA anion is a little faster than MSA anion.

### Calculating the Column Capacity

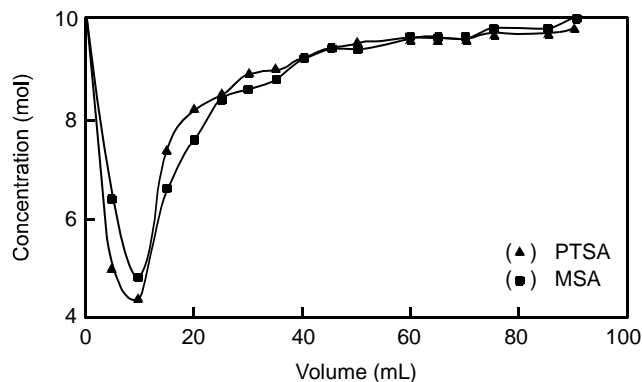
By determining the amount of Cl<sup>-</sup> released from the column until its content in the column reaches  $\leq 0.001$  mmol. The total exchangeable Cl<sup>-</sup> for each acid in 2 g PANi coated silica gel was calculated and it was 0.118 mmol Cl<sup>-</sup> for PTSA and 0.115 mmol Cl<sup>-</sup> for MSA. Thus the column capacity for PTSA is  $0.118/2 = 0.059$  meq/g and  $0.115/2 = 0.057$  meq/g for MSA. In Figure 3 the graphs of [PTSA] and [MSA] versus the volume of chloride ion (mL) passed through column are plotted. In these diagrams the break through points for each acid in a column of polyaniline coated silica gel with (L/D) of 5/1 cm are shown.



**Figure 1.** The calibration curve of absorbance versus [Cl<sup>-</sup>] for spectrophotometric method.



**Figure 2.** Chloride ion concentration released versus PTSA and MSA (mL) entered the column.



**Figure 3.** Concentration of PTSA and MSA entered versus chloride ion (mL) released the column.

### Conductivity Studies

Conductivity of the polymer depends on the length of conjugated double bonds on the chain of polymer and the kind of dopant agent. So we have investigated the conductivity of silica gel coated PANi before and after anion exchange. Anions (dopant agents) on conducting polymers are exchangeable with other anions and produce polymers with different conductivities. The counter ion has an important role in the conductivity of conducting polymers. In this work exchange of  $\text{Cl}^-$  ions with the more stable ions such as sulphonates would increase the conductivity. The exchange is very rapid and the more stable ions take the place of the less stable ions. Regeneration of the column is possible by increasing the concentration of the less stable ion in longer periods of time. Table 3 shows the conductivity of PANi coated on silica gel before and after anion exchange.

### CONCLUSION

The anion-exchange process of two sulphonic acid derivatives, PTSA and MSA, with  $\text{Cl}^-$  of doped polyaniline is quantitative up to 0.005 M concentration of both acid and this is not affected by flow rates of acids up to 4.6 mL/min. However, PTSA anion shows little faster anion-exchange rate than MSA anion. The calculated column capacity was 0.059 meq/g and 0.057 meq/g for PTSA and MSA, respectively. Also the exchange of  $\text{Cl}^-$  with sulphonate anions increases the conductivity of the polymer.

### REFERENCES

1. Stejskal J. and Gilbert R. G., Polyaniline, preparation of conducting polymer, *Pure Appl. Chem.*, **74**, 857-867 (2002).
2. Prokes J. and Krivka J., Enhanced stability of polyaniline/inorganic salt composites during temperature cycling, *Polym. Deg. Stab.*, **68**, 261-269 (2000).
3. Anand, J., Palaniappan, S., and Sathyanarayana, D.N., Conducting polyaniline blends and composites, *Prog. Polym. Sci.*, **21**, 993-1002 (1998).
4. Tallman D.E., Pae Y., Chen G., Wierwagen G.P., Reems B., and Gelling V.J., *Conductive Polymer and Plastic in Industrial Application*, 201-211, (1999)
5. Hosseini S.H. and Entezami A.A., Preparation and characterization of polyaniline blends with polystyrene, poly(vinyl chloride) and poly(vinyl acetate) for toxic gas sensors, *Polym. Adv. Technol.*, **12**, 482-493 (2001).
6. Hosseini S.H. and Entezami A.A., Conducting polymer blends of polypyrrole with polystyrene poly(vinyl chloride) and poly(vinyl acetate) based toxic gas sensors, *J. Appl. Polym. Sci.*, **90**, 49-62 (2003).
7. Wang J., Anion exchange nature of emeraldine base (EB) polyaniline and a revisit of the EB formula, *Synth. Met.*, **132**, 49-52, (2002).
8. Wang J., Polyaniline coating: Anion membrane nature and bipolar structures for anticorrosion, *Synth. Met.*, **132**, 53-56 (2002).
9. Niwas R., Khan A.A., and Varshney K.G., Synthesis and ion exchange behaviour of polyaniline Sn(IV) arsenophosphate, *Coll. & Surf. A*, **150**, 7-14 (1999).
10. Armes S.P., Gottesfeld S., Beery J.G., Garzon F., and Agnew S.F., Particle sizing by DCP and its role in colloidal polymer chemistry, *Polymer*, **32**, 2325-2334 (1991).
11. Stejskal J., Quadrat O., and Sapurina I., Polyaniline coated silica gel, *Eur. Polym. J.*, **38**, 631-637 (2002).
12. Kim B.J., Oh S.G., Han M.G., and Im S.S., Preparation of polyaniline nanoparticles in micellar solutions as polymerization medium, *Langmuir*, **16**, 5841-5845 (2000).
13. Alberti G., Casciola M., Dianigi C., and Vivani R., Chromatograph and ion-exchange separation, *Proc. Int. Conf. on Ion Exch.*, ICIE, 95, Takamatsu, Japan, 95 (1995).
14. Epstein A.J., Joo J., Wu C.-Y., and MacDiarmid A.G., *Intrinsically Conducting Polymer: An Emerging Technology*, M. Aldissi, (Ed.), Kluwar, Netherlands, 165 (1993).