Ion Exchange Properties and Kinetic Behaviour of Polyaniline-coated Silica Gel for \(p\)-Toluenesulphonic Acid and Methanesulphonic Acid

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A B S T R A C T

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 micropipette 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
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, SiO₂ with PANi hydrochloride. The deposition of thin PANi and PPy coating onto monodisperse silica particles of 1 m diameter was reported by Armes et al. [10]. Stejskal and co-worker [11] prepared PANi in the presence of silica having 7 m 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 m in size [12]. Also 60-125 m 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].

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 dessicator over solid KOH and CaCl₂. 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 4Å, 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, SiO₂, 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, (NH₄)₂S₂O₈, 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 G₂ 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 NH₄OH, 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⁻ ion by immersing into 100 mL HCl 1M solution. Then it was filtered and washed to remove the excess acid and Cl⁻ anion. It
is notable that due to the release of trace amounts of doped Cl\textsuperscript{-} 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 Cl\textsuperscript{-} anion by AgNO\textsubscript{3} 0.05 M solution until it was confirmed that there was no Cl\textsuperscript{-} 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 Cl\textsuperscript{-} anion in the polymer is exchanged by \textit{p}-toluenesulphonate anion and Cl\textsuperscript{-} anion is released. The amount of Cl released due to anion-exchange was determined by the Volhard’s back titration method with a micropippet. 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 Cl\textsuperscript{-} 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 Cl\textsuperscript{-} 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 Cl\textsuperscript{-} 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 Cl\textsuperscript{-} 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 [Cl\textsuperscript{-}] by spectrophotometric method, first several standard solutions of 10, 20, 30, 40 and 50 ppm of Cl\textsuperscript{-} in acetone were prepared. Then 2 mL of distilled water, 0.4 mL of ferric ammonium sulphate [(SO\textsubscript{4})\textsubscript{3}Fe\textsubscript{2} (NH\textsubscript{4})\textsubscript{2}(SO\textsubscript{4}).2H\textsubscript{2}O] solution in nitric acid 9 M, 0.4 mL of saturated solution of mercury(II) thiocyanate, Hg(SCN)\textsubscript{2} in ethanol was added to each sample.

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

<table>
<thead>
<tr>
<th>[PTSA] or [MSA] M</th>
<th>V (mL)</th>
<th>PTSA or MSA entered the column (mmol)</th>
<th>Flow rate (mL/min) (±0.05)</th>
<th>Released Cl\textsuperscript{-} (mmol) (±0.001)</th>
<th>Exchange percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0025</td>
<td>5</td>
<td>0.0125</td>
<td>0.5</td>
<td>0.0125</td>
<td>100</td>
</tr>
<tr>
<td>0.005</td>
<td>5</td>
<td>0.025</td>
<td>0.5</td>
<td>0.025</td>
<td>100</td>
</tr>
<tr>
<td>0.01</td>
<td>5</td>
<td>0.05</td>
<td>0.5</td>
<td>0.045</td>
<td>90</td>
</tr>
<tr>
<td>0.02</td>
<td>5</td>
<td>0.1</td>
<td>0.5</td>
<td>0.076</td>
<td>76</td>
</tr>
<tr>
<td>0.005</td>
<td>5</td>
<td>0.025</td>
<td>1</td>
<td>0.025</td>
<td>100</td>
</tr>
<tr>
<td>0.005</td>
<td>5</td>
<td>0.025</td>
<td>2.28</td>
<td>0.025</td>
<td>100</td>
</tr>
<tr>
<td>0.005</td>
<td>5</td>
<td>0.025</td>
<td>4.6</td>
<td>0.025</td>
<td>100</td>
</tr>
</tbody>
</table>
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\textsuperscript{-}] 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\textsuperscript{-} 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\textsuperscript{-} ion by Cl\textsuperscript{-} ion. This will produce a colourful [Fe(SCN)]\textsuperscript{2+} complex in the presence of Fe\textsuperscript{3+} ion. The intensity of the colour depends on the Cl concentration.

2Cl\textsuperscript{-} + Hg(SCN)\textsubscript{2} + 2Fe\textsuperscript{3+} \rightleftharpoons HgCl\textsubscript{2} + 2[Fe(SCN)]\textsuperscript{2+}

**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\textsuperscript{-} 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\textsuperscript{-} released due to ion exchange was determined by the Volhard’s back titration method in each.

**Scheme I.** Structure of different forms of polyaniline.
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−] in each sample the graph of [Cl−] 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− 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− anions of the polymer have been released. So the total exchangeable Cl− ions of the polymer can be calculated. It is notable that the first 5 mL leaving the column has no Cl− 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− released from the column until its content in the column reaches ≤ 0.001 mmol. The total exchangeable Cl− for each acid in 2 g PANi coated silica gel was calculated and it was 0.118 mmol Cl− for PTSA and 0.115 mmol Cl− 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.
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 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 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 Cl\(^-\) with sulphonate anions increases the conductivity of the polymer.

REFERENCES