Synthesis, Characterization and Adsorption Studies of Sulfonated Poly(Styrene)

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Summary: Poly(styrene) was synthesized by suspension polymerization of styrene. Molar mass of poly(styrene) was determined by viscosity method. Sulfonated poly(styrene) was synthesized by direct sulfonation of poly(styrene) at 40°C. These products were identified by using IR spectroscopic technique. Cation exchange properties of sulfonated poly(styrene) have been determined for some metal ions such as Ni^{2+}, Zn^{2+}, Cu^{2+} and Ca^{2+}. The distribution co-efficient and apparent adsorption capacities show that selectivity order of the metals as follow: $Ni^{2+} > Zn^{2+} > Cu^{2+} > Ca^{2+}$. It was found that by increasing the pH of solution, the distribution Co-effecients (Kd) value also increased.

Key words: Poly (styrene), Metal ions, Adsorption.

Introduction

In the last few decades the roles of porous material have received considerable attention due to their application in the field of adsorption, cation exchange, catalysis and as low dielectric constant materials [1]. Presently, the studies of highly ordered macro porous materials have become a burning issue in the field of polymer chemistry. These materials possess some diagnostic characteristics suitable for fabrication of photonic band–gap crystals [2, 3].

Various polymers when used as ion-exchangers have been the subject of considerable interest for analytical chemists and chemical engineers due to their high resistance to temperature extremes and swelling. Ion exchange behavior of polymers has been studied and was found very useful for their selective behavior for certain ions or group of ions. Sulfonic acid polymers can be utilized as best system for these studies because of their maximum charge density, minimum adsorptive sites and strongly acidic exchange group [4].

Previously our group has reported adsorption capacity of polyaniline composites for Cr^{3+}, Pb^{2+} [5], and Ni^{2+}, Cu^{2+} ions [6]. Similarly we have also reported the adsorption studies of Cr^{3+} with different copolymers of sulfonated poly(styrene) [7]. In continuation of our previous work, we report here the cation exchange studies of Ni^{2+}, Zn^{2+}, Cu^{2+} and Ca^{2+} using sulfonated poly(styrene) material.

Experimental

Metal Used

All the chemicals and solvents used were of analytical grade; Styrene, Benzoyl Peroxid, Polyvinyl alcohol water, 5% NaOH solution, Nitrogen gas, 98% H_2SO_4, Phosphorus Pentoxide (P_2O_5), Poly(styrene), Cyclohexane, Crushed ice, Ammonia(aq), Hydrochloric Acid, Salts of metals ($NiSO_4 \cdot 7H_2O$, $CaSO_4 \cdot 2H_2O$, $ZnSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$) were procured from Merck/BDH company. I.R. spectra were recorded on Perkin Elmer A-100 FTIR spectrophotometer.

Synthesis of Poly(styrene)

Poly(styrene) was prepared by suspension polymerization of styrene at 80°C, dried and subjected for FTIR analysis. Average molar mass was also determined by viscosity method using Mark-Howink-Sakurada equation [8, 9].

Synthesis of Sulfonated Poly(styrene)

Sulfonated poly(styrene) was prepared by direct sulfonation of Poly(styrene). For this purpose 50 ml of H_2SO_4 (98%) was transferred to a 500 ml round bottom flask. 10 g of P_2O_5 was slowly added with stirring. Reaction mixture was cooled at 40 °C. 1.5 g of poly(styrene) was dissolved in 25 ml cyclohexane and added drop wise to acid solution. After 30 minutes reaction was stopped from stirring and allowed to stand for 1 hour at 40°C. Reaction mixture was cooled by adding 25 g of crushed ice with constant stirring. Sulfonated poly(styrene) was precipitated in the form of stick mass. Mixture was separated and acid was added to 100 ml of distilled water, filtered and dried at 40°C for 72 hours.

Adsorption Studies

7 buffer solutions of different pH were prepared. The distribution Co-effecients (Kd) of the metal ions have been determined by batch

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equilibrium technique at 25°C. The amount adsorbed was determined from the difference between initial and final concentration in clear supernatant solution using spectrophotometric methods [10, 11]. A column (8 x 0.8 cm) was set in vertical position and a pad of glass wool was placed in its porous bed to support the resin. A thick slurry of the ion exchanger in water was prepared and poured into the column followed by washing with 6 N HCl and then treating with distilled water to remove lost traces of undesirable ions.

Results and Discussion

In contrast to the low molar mass compounds, a polymer is usually a complex mixture of molecules of different molar masses. The polymers are thus disperse and heterogeneous in composition. Therefore the molar mass of a polymer is actually an average of the molar masses of constituent molecules. Different averages are obtained depending on the method of measurement of the molar mass [8]. Here in the present studies molar mass of the prepared poly(styrene) was found to be 5.4×10^5 g/mole, which was determined by using viscosity method.

IR spectra of pure poly(styrene) and sulfonated poly(styrene) are shown in Figures 1 & 2 respectively. IR spectrum of poly(styrene) was taken by forming a thin film of poly(styrene) by dissolving it in chloroform and of sulfonated poly(styrene) was taken in the form of transparent pallets with potassium bromide using Perkin Elmer A-100 FTIR spectrophotometer.

The most important vibration bands, which allow the identification of poly(styrene) are summarized as follow, the peak at 1600 cm^{-1} results from the vibrations of aromatic ring of styrene. A strong absorption band at 3058 cm^{-1} results from the vibrations of $-CH=CH_2$ group of styrene. Peaks located at 757 cm^{-1} and 1492 cm^{-1} indicate the presence of C-H of the aromatic poly(styrene) and C-$C_{stretch}$ in the aromatic ring of poly(styrene), respectively. Hence in the case of sulfonated poly(styrene) prepared by direct sulfonation of poly(styrene) a strong adsorption band centered at 1200 cm^{-1} is the asymmetric stretching vibration of the O=S=O unit of sulfonated poly(styrene). The peak at 1052 cm^{-1} [12, 13] results from the vibrations of phenyl ring substituted with a sulfonic group. Sulfonic acid peak located at 1375 cm^{-1} indicates the deprotonation of the sulfonic acid. These results suggest that the $-SO_3H$ group when attached with poly(styrene), it forms the sulfonic cation in acidic medium. Hence sulfonated poly(styrene) acts as cation exchanger for a number of metals. Our results are in agreement with the literature [14].

Different eluents having pH 2 – 10 were prepared. Various solutions having concentration of 2.5×10^{-3} M were prepared for each metal ion (Ni^{2+}, Zn^{2+}, Cu^{2+} and Ca^{2+}) and their presence in the solution was estimated by spectrophotometric method. Distribution coefficient (Kd) of each metal ion was determined by using the batch equilibrium technique (Table 1). Ion exchange for metal ions under investigation clearly proved that distribution coefficient is highly dependent on the pH of its solution and enormously increases with the rise of pH, as shown in Figures 3 and 4 for metals (Ni^{2+}, Zn^{2+}, Cu^{2+} and Ca^{2+}). The order was found to be $Ca^{2+} < Cu^{2+} < Zn^{2+} < Ni^{2+}$. The order is approximately in accordance with acidity of the metal and its crystal lattices. This phenomenal behavior may be due to the fact that metal with a large atomic number are adsorbed more strongly as compared with those having low atomic number. Under these conditions nickel is strongly held at the surface of sulfonated poly(styrene).

Kd values for each metal ion was determined depending on the pH of solution, which proved that various ions under investigation could be easily separated into Ni^{2+}, Zn^{2+}, Cu^{2+} and Ca^{2+}. This fact was confirmed by the column technique experiments that the separation of these ions was possible by proper control of pH. For instance continuous column elution with pH 7.9, 7.0, 4.5 and 3.0 successively categorized the ions in different groups (Ni^{2+}, Zn^{2+}, Cu^{2+} and Ca^{2+}) as shown in Fig. 4. This proved that sulfonated poly(styrene) has high affinity for nickel, and with other metals being in order $Ni^{2+} > Zn^{2+} > Cu^{2+} > Ca^{2+}$ and that affinity is dependent upon the solution of pH and counter ion. However the mechanism associated with ions exchange on sulfonated poly(styrene) has not so far been clearly understood.

Table-1: Kd values of Ni^{2+}, Zn^{2+}, Cu^{2+} and Ca^{2+} metal ions at 40°C on sulfonated poly(styrene).

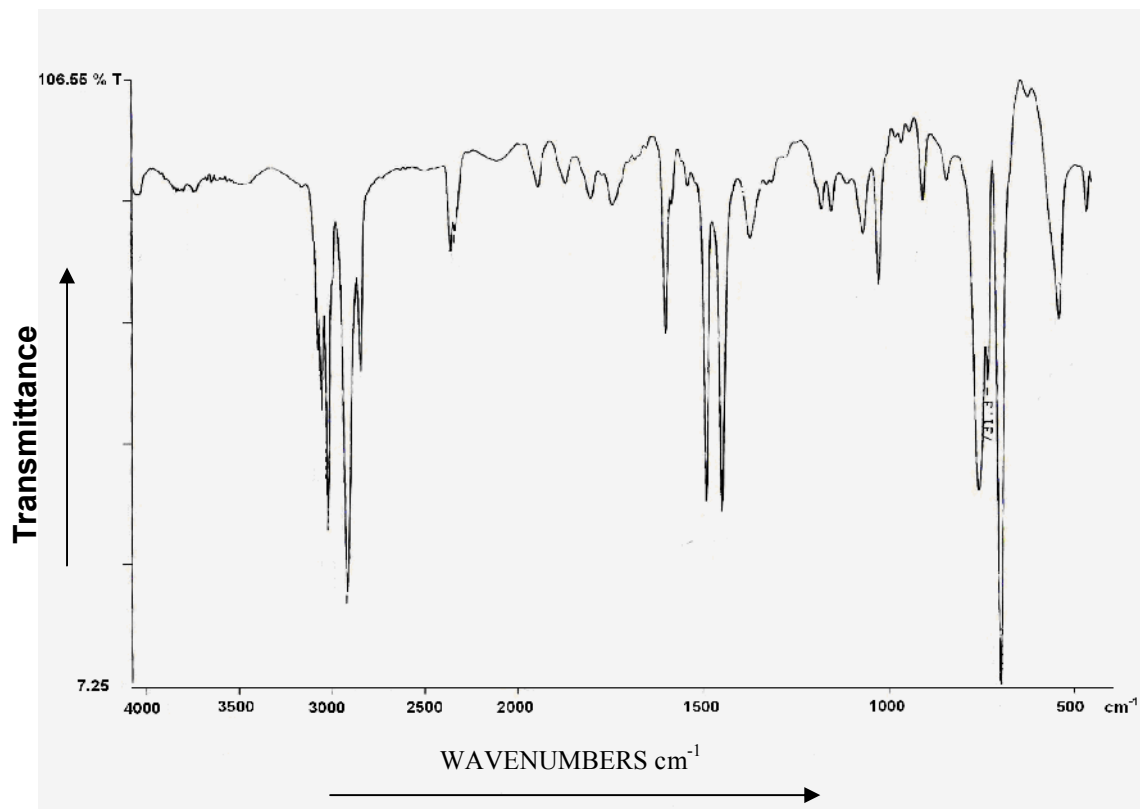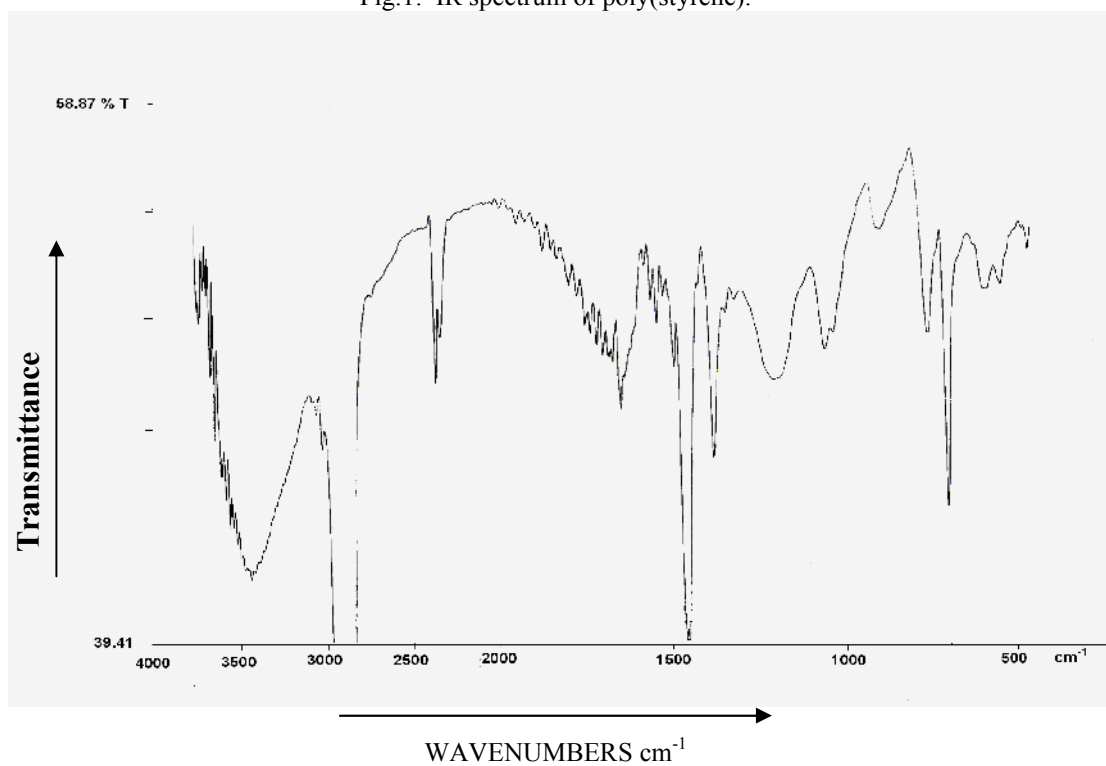| Ni^{2+} Ion						
Final pH of soln.	5.0	6.0	6.4	7.0	8.6	9.8
Kd value	177	316	380	525	941	1150
Zn^{2+} Ion						
Final pH of soln.	4.5	6.1	6.5	7.1	8.1	9.2
Kd value	150	163	180	212	284	303
Cu^{2+} Ion						
Final pH of soln.	2.2	3.8	5.2	6.2	7.0	8.5	9.4
Kd value	25	31.5	56	66	72	92	172
Ca^{2+} Ion						
Final pH of soln.	2.2	4.5	6.1	6.8	7.4	8.2	9.8
Kd value	2.01	4.16	13.63	19.04	31.57	47.05	56.25

Fig.1: IR spectrum of poly(styrene).
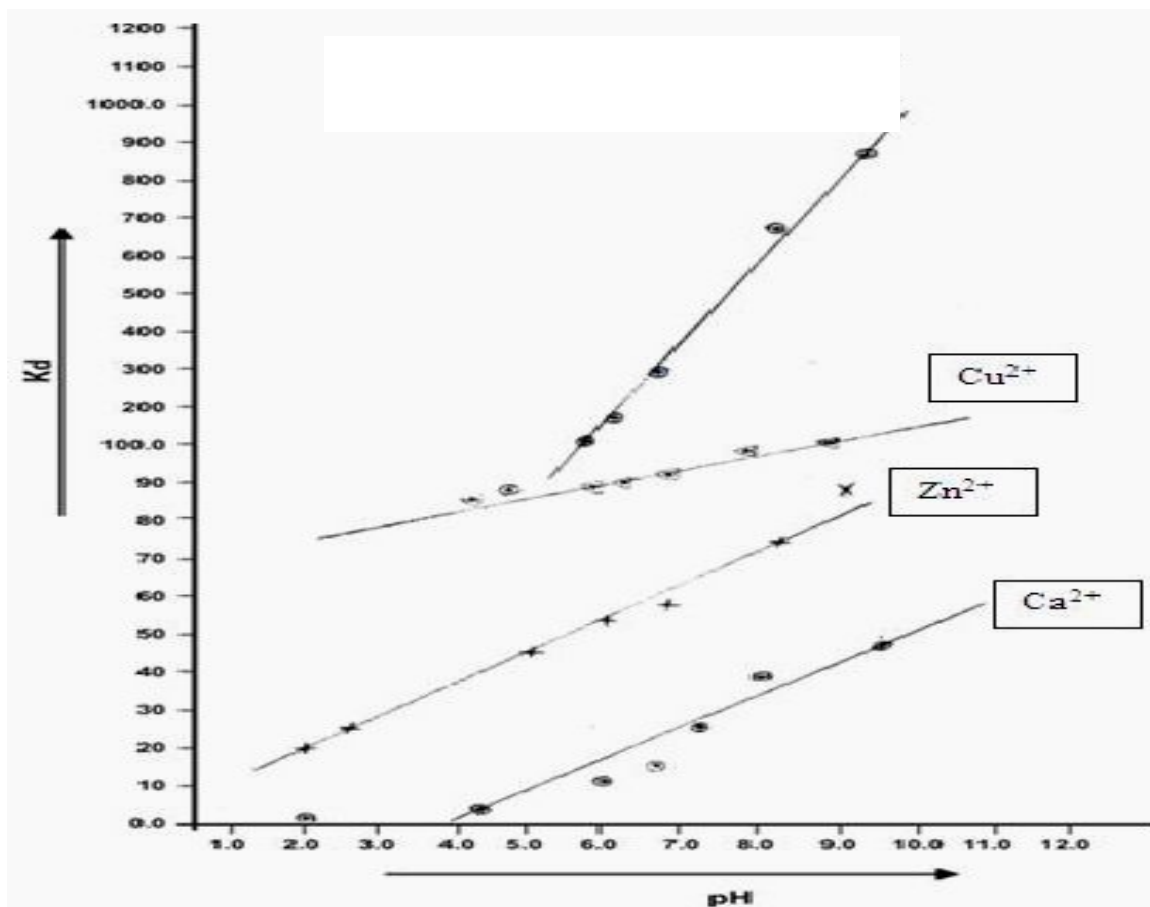

Fig. 2:   IR spectrum of sulfonated poly(styrene).

Fig. 3:   Cross plot of pH versus Kd for the comparison of Ni^{2+}, Zn^{2+}, Cu^{2+} and Ca^{2+} metal ions.
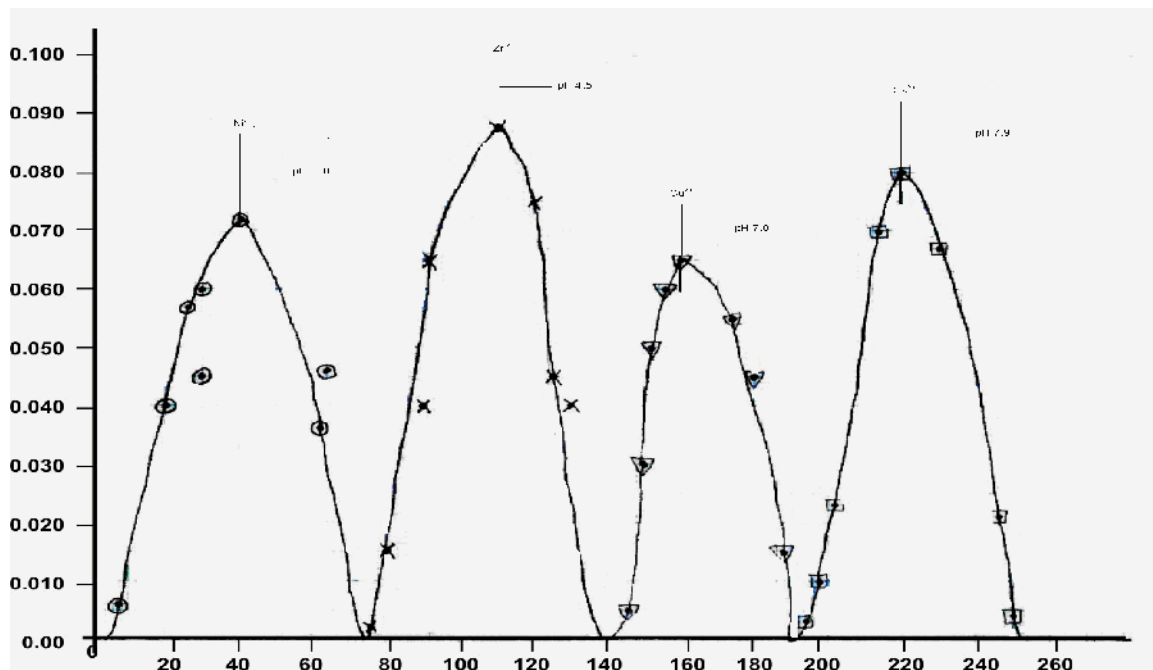

Fig. 4:   Elution curves by various pH with sulfonated poly(styrene) dried at 40°C.

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