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PREPARATION OF HIGH CAPACITY CHLOROETHYLATED STRONG BASE ANION EXCHANGE RESIN USING NO_x

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ABSTRACT

Suspension polymerization of styrene and divinylbenzene has been carried out in the presence of gelatin as stabilizer to form macroporous polystyrene divinylbenzene resin (PS–DVB). In order to prepare surface chloroethylated macroporous PS–DVB resin, it is nitrated (resin 2) using a mixture of NO and NO_2 gases (called NO_x), is reduced to amine groups (resin 3), further reacted with dichloroethane, then quarternized (resin 6) using trimethyl amine. Simple material balance demonstrates that all NO_x reacted show up as exchanging sites of resin 6 and this resin has at least three exchanging sites on every repeat unit.

We have examined the effect of duration of nitration on the exchange capacity of resin 6 and it was found that it first increased with increase in the duration of nitration, reaching a broad maxima of 4.8 meq/g of wet resin with 69% moisture (or capacity of 15.5 meq/g of dry resin) for about 5 hr of nitration and when nitration is continued for a longer time there is a fall due to polymer degradation. This is to be compared with the commercial

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chloride form of strong base anion exchange resin, which has the exchange capacity of 1.68 meq/g of wet resin with 43.53% moisture (or capacity of 2.97 meq/g of dry resin). In order to assess the solvation ability of the chloroethylated resin, we evolved a three-stage drying procedure and showed that it holds moisture differently. On a dry gram basis, the chloroethylated resin is about five times superior compared to available commercial resin.

INTRODUCTION

Exchangers are insoluble solid materials that carry either chelating functional groups, cations, or anions, or all the three. Among all these, the most important are organic exchangers, which are crosslinked polymer gels (1–5). The properties of these gels arise because of the functional groups in them and these are created in the polymer gel by chemical reactions. These could be obtained by (a) polymerizing functional monomers, (b) grafting of a second functional monomer on an already prepared polymer, followed by second stage polymerization, (c) immobilizing suitable organic reagents, and (d) polymerizing nonfunctional monomers followed by their modification. The organic material most commonly used is a copolymer gel of styrene and divinylbenzene (denoted by PS–DVB) and the general purpose resin contains about 8–25% of the latter.

Commercially, the PS–DVB copolymer resin is preferred because of the fact that these have preponderance of phenyl rings, which can be functionalized easily. All functionalizing reactions reported in the literature are found to be liquid phase reactions in which penetration of reagents into the polymer as well as the pores of the resin is extremely important. The common starting point of these reactions invariably is the chloromethylation in which $-CH_2Cl$ groups are generated using an extremely carcinogenic reagent chloromethyl methyl ether (CMME). The overall reaction is not efficient and about 2% chloromethyl groups per gram of resin is all that can be obtained.

In this paper, we report a gas phase nitration of macroporous PS–DVB copolymers, using a mixture of NO and NO_2 gas (sometimes called NO_x) at relatively low temperatures and this has not been reported in literature. For the purpose of anion exchange resins, aminated resin can be formed easily by reducing these nitrated functional groups with hydrazine hydrate. The resin thus formed can also serve as a reasonable starting point for more advanced modifications. Since the modification carried out in this work is a gas phase reaction involving NO_x with the copolymer resin, the availability of the reagents within it is not expected to be the limiting step. In order to assess the efficacy of this gas phase reaction, we have converted these into anion exchange resins and

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compared it with the commercially available resin (a chloride form of strong base anion exchanger obtained from Dow Chemicals). We have found the exchange capacity of our resin to be about five times more than that of commercial resins, indicating high efficiency of the gas phase nitration technique.

EXPERIMENTAL SECTION

Preparation of Macroporous Resin

In order to get large particles of PS–DVB co-polymer resins, suspension polymerization technique has been used (6–9). In this study, organic phase was prepared by mixing styrene (280 g, 3.04 g mol), DVB (80 g, 0.62 mol), azobisisobutyronitrile (4 g, 0.02 mol), and toluene (200 g, 2 mol). This organic phase was suspended in an aqueous solution containing distilled water (900 mL), sodium sulfate (48 g, 0.034 g mol), calcium carbonate (8 g, 0.08 mol), and gelatin (0.028 g).

The suspension polymerization process is carried out under controlled stirring at 60 ± 2°C for 4 hr in a setup shown in Fig. 1. After this time, the temperature of the reaction mass is increased to 90 ± 2°C in half an hour and then it is kept constant for the next 2 hr. These resins now have considerable mechanical strength and are separated and washed with water. To remove excess calcium carbonate, 0.1 *N* HCl solution is added to the resin. Again resin is separated, washed with water and finally with methanol, and is dried in an oven maintained at 70–75°C. During experimentation, gelatin content in the aqueous phase is found to play an important role in controlling the particle size of resin and it is found that the average particle size as well as the internal surface area of the resin tends to decrease with the increase in gelatin content.

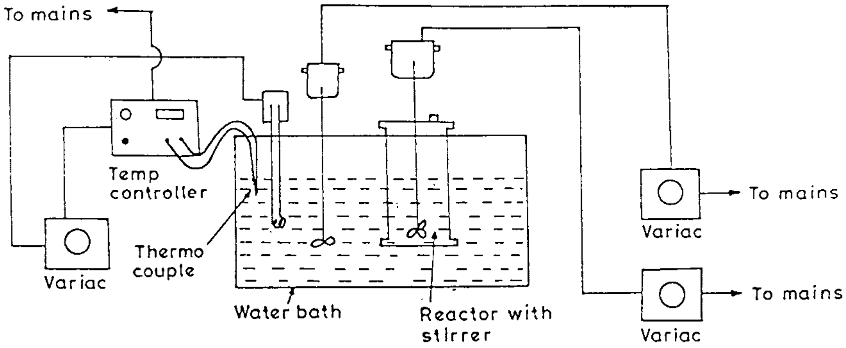
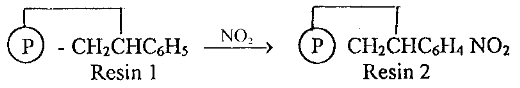


Figure 1. Experimental setup for the preparation of PS–DVB resin.

Gas Phase Nitration of Polystyrene Divinylbenzene Resin Using NO_x

Direct gas phase nitration of PS–DVB resin occurs with extreme efficiency in the presence of a small amount of NO and is carried out in a 2.5 L reaction bottle. This reaction vessel is equipped with an aluminum cap with a 1.2 mm opening at the top for injecting the gas, which is closed by a silicon rubber septum. Using the method of Refs. (10–13), a mixture of NO and NO_2 (called NO_x) is generated in a 1.5 L, two neck round bottom flask by reacting sodium nitrite $NaNO_2$ (10 g, 0.14 g mol) with sulfuric acid (H_2SO_4 sp.gr. 1.18, 25 mL) in the presence of ferrous sulfate $FeSO_4$ (5 g, 0.072 g mol). The flask is equipped with a rubber septum for withdrawing NO_x with the help of a 100 mL syringe.

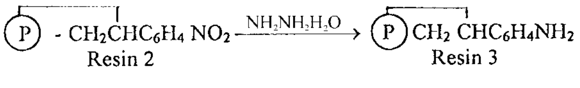
Approximately 1.5 g of PS–DVB resin is introduced into the reaction vessel and is placed in the oven, maintained at the desired reaction temperature. A small needle is punctured through the silicon septum of the reactor vessel to allow a thermal equilibrium with the oven. The gas inside the bottle expands due to heating and escapes through the needle. After this, the needle is removed; the vessel is taken out and allowed to cool at room temperature. This creates slight vacuum inside the vessel so that when NO_x is introduced into the bottle, at the reaction temperature, the total pressure remains approximately at 1 atm. After feeding the required amount of gas mixture, the vessel is again kept in the oven maintained at the reaction temperature. After completion of nitration, the vessel is taken out from the oven and allowed to cool to room temperature for withdrawing the resin for analysis. If we represent a repeat unit of PS–DVB by resin 1 below, the nitration of the resin can be written as



$$\underset{\text{Resin 1}}{Ⓟ\text{-}CH_2CHC_6H_5} \xrightarrow{NO_2} \underset{\text{Resin 2}}{Ⓟ\,CH_2CHC_6H_4NO_2} \qquad (1)$$

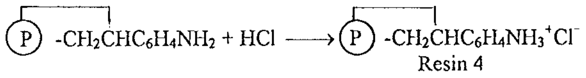
Preparation of Chloroethylated Anion Exchanger, Resin 6

Amination of nitrated PS–DVB resins is carried out with hydrazine hydrate. A measured amount of 1.5 g of resin 1 is placed in a conical flask with 50 mL of hydrazine hydrate. The reaction mass is maintained at 50°C for 4 hr in an oil bath maintained at 60°C. After the reaction is over, the resin is filtered, then washed properly with distilled water and dried, and the overall reaction can be represented by



$$\underset{\text{Resin 2}}{Ⓟ\text{-}CH_2CHC_6H_4NO_2} \xrightarrow{NH_2NH_2H_2O} \underset{\text{Resin 3}}{Ⓟ\,CH_2CHC_6H_4NH_2} \qquad (2)$$

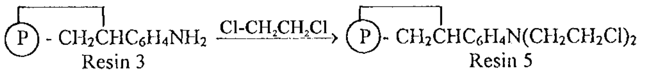
Experiments show that resin 3 exchanges with chloride ion only once as follows.



$$\text{(P)-}CH_2CHC_6H_4NH_2 + HCl \longrightarrow \text{(P)-}CH_2CHC_6H_4NH_3^+Cl^- \quad \text{(3)}$$

Resin 4

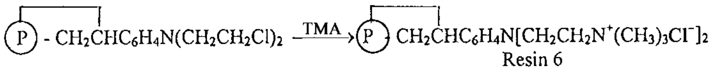
Resin 4 cannot be regenerated using the American Society for Testing and Materials (ASTM) procedure. As a result, resin 3 is first chloromethylated and then quaternized to a strong base anion exchange resin as follows. Approximately, 1.5 g of resin 3 is refluxed with 50 mL of 2% v/v solution of dichloroethane in ethanol for 4 hr to give



$$\text{(P)-}CH_2CHC_6H_4NH_2 \xrightarrow{Cl\text{-}CH_2CH_2Cl} \text{(P)-}CH_2CHC_6H_4N(CH_2CH_2Cl)_2 \quad \text{(4a)}$$

Resin 3 Resin 5

After this modification, 1.5 g of dried resin 5 is refluxed with 5% v/v trimethyl amine (TMA) in ethanol for 4 hr. The reaction occurring can be written as



$$\text{(P)-}CH_2CHC_6H_4N(CH_2CH_2Cl)_2 \xrightarrow{TMA} \text{(P)}CH_2CHC_6H_4N[CH_2CH_2N^+(CH_3)_3Cl^-]_2 \quad \text{(4b)}$$

Resin 6

Determination of Exchange Capacity of Resins 3 and 6

We have determined the exchange capacity of resins 3 and 6 by two procedures. The titration method is simpler but underestimates the result, and there is more scatter in the exchange capacity data.

Titration Method

This method is based on the fact that all amine groups would react with HCl to give ammonium salt. In view of this, the procedure consists of placing approximately 1.5 g of resin 3 in a conical flask and refluxing it with 50 mL of 0.1 *N* HCl for 4 hr. The reaction mass is then filtered and the filtrate contained unconsumed HCl, which is titrated with 0. *N* NaOH to determine the chlorine ion intake by the aminated resins. This always gives a lower value compared to gravimetric method.

Gravimetric Method

The method of determining exchange capacity of resin given in ASTM standard no. ASTMD (2187, 2687, 3087, 3375) is the gravimetric method consisting of the following two steps (14).

(a) *Regeneration step*. In this, first mixed acid is prepared by mixing 18.1 mL of H_2SO_4 (sp.gr. 1.84) with 27.5 mL of HCl (sp.gr. 1.19) in 500 mL of distilled water. The entire content is made up to 1000 mL using distilled water. After this, the test water is prepared by diluting the mixed acid with distilled water up to 1% concentration. This test water is then added to resin 3 (or resin 6) in a quantity of 100 mL per gram and kept for 24 hr. After this, the resin is filtered and washed with distilled water till the filtrate becomes neutral, which is concluded by observing whether the color of methyl orange changes from orange red to orange yellow or not. This way we get the resin, which is free from the mixed acid.

(b) *Determination of capacity*: The regenerated resin obtained from step (a) is then mixed with 0.1 *N* $NaNO_3$ solution (8.5 g in 100 mL distilled water) and kept for another 24 hr. Then the reaction mass is filtered and the filtrate is added to 1.7 g of $AgNO_3$ with 2–3 drops of HNO_3 and the entire mass is kept for 24 hr. The chlorine ions present in the filtrate form AgCl, which is precipitated. This precipitate is filtered, weighed, and the capacity of aminated resin is calculated.

Elemental Test for Nitrogen Detection in Polystyrene Divinylbenzene Resin

In order to detect nitrogen in resins 2 and 3, the Lassaigne element spot detection test has been modified slightly. In this, element nitrogen is detected by fusing the polymer resin with metallic sodium to form sodium cyanide. After the fusion reaction is complete, the entire content is washed with water, and 2–3 mL of the filtrate solution is poured into a test tube containing 0.1–0.2 g of powdered iron (II) sulfate crystals. The mixture is then heated gently with shaking, and without cooling dilute sulfuric acid is added to dissolve the metallic hydroxides. A Prussian blue color of the mixture formed confirms the presence of nitrogen.

Bond Energy Determination Through Electron Spectroscopy for Chemical Analysis

The instrument used in this study is electron spectroscopy for chemical analysis (ESCA) VG MK.II by VG Scientific, UK. For determining the binding energy of different elements present in PS–DVB resins, the sample is first baked for 8–10 hr at 100°C. After proper baking, the sample is introduced to the sample holding track/tray in the main chamber by sample transport mechanism. Our sample is in the form of 1 mm size resin and the survey scan is taken in the two regions of 0–500 and 500–1000 eV, respectively. As per the survey scan and depending upon the nature of modifications carried out, various peaks of different elements are obtained. With the information available from standard samples, each element is scanned individually for different binding energy ranges. In our case, the elements scanned are carbon, nitrogen, and oxygen. This gives rise to their respective peaks along with their binding energy regions in the survey scan. Thereafter, in order to analyze the binding energy of a particular element and its shifting from its standard value, sample depth scan is taken individually for carbon in the range 275–325 eV, for oxygen in the range 525–575 eV, and for nitrogen in the range 400–450 eV. The entire analysis is carried out for blank, nitrated, and aminated resins.

RESULTS AND DISCUSSION

The study of this paper is divided into five sections and consists of (a) the formation of resins by suspension polymerization, (b) chemical characterization of the nitrate and amine functional groups in the resin, (c) the time and temperature effects of nitration, (d) solvation effect of modification, and (e) effect of modification on surface area and morphology. These are individually discussed below.

Suspension Polymerization of Crosslinked Macroporous Resin

In this study, crosslinked macroporous PS–DVB copolymer resin in the form of spherical beads are prepared as per the recipe given in “Preparation of Macroporous Resin”. It is macroporous in nature because of the use of toluene as a diluent in the organic phase, which is a good solvent for linear polystyrene chains. Resin 1 has been characterized for its particle size distribution and internal surface area by varying the amount of different ingredients, the nature and fraction of diluent, and the amount of gelatin in the recipe. In this work we have changed the nature of the diluent by mixing *n*-heptane (which is a nonsolvent to linear polystyrene) with toluene as the solvating medium. To determine the effect of this ratio on the internal surface area and particle size distribution of the resins formed, the internal surface area measurements have been made using standard BET isotherm apparatus (Pulse Chemisorb 2770) and results are summarized in Table 1. It is observed that the suspension polymerization technique of forming polymer resins cannot be used beyond

Table 1. Effect of Nature of Diluent on the Internal Surface Area

Percentage Heptane	Internal Surface Area (m^2/g)
0	9.88
10	6.33
20	5.03
30	3.86
40	Organic and water layer demix and polymer formed in one lump

40% heptane and as the percentage of heptane is increased, the internal surface area is reduced. In the presence of a solvating diluent toluene, the formed resin is in the swollen state and its degree of swelling reduces by the presence of a nonsolvent. In the case of a nonsolvent diluent, the polymer chains are more entangled and thus form a compact structure with lower internal surface area. The particle size distribution is measured by sieving and is extremely sharp, and its shape is not found to be affected by the percent ratio of the nonsolvent *n*-heptane present. The average particle size goes down as the amount of *n*-heptane increases and the reason for this is not quite clear.

In the next phase of the study, only toluene is used as the solvating medium and the effect of gelatin content in the aqueous phase has been examined. It is found that this plays a major role in the particle size distribution as well as the internal surface area of the resin. The experiments are conducted using different gelatin contents in different runs, and the particle size distribution obtained for each run is found to be extremely sharp. It is found that increasing gelatin content reduces the average size of resins and results are shown in Fig. 2. Experiments show that there is a critical gelatin concentration, C_{crit}, below which the resin forms an agglomerate to give a large polymer mass.

Internal surface area of the resin formed is another property, which is influenced by the amount of gelatin content in water. It is found that the internal surface area increases with the increase in gelatin content, and it is seen that there is an optimal value of gelatin content for which the average size of particle and internal surface area, both give optimal performance. In this study, the value of gelatin content is chosen as 0.028 g/100 mL of water, which gives an average particle size of 1 mm and an internal surface area of 9.879 m^2/g (see Table 2).

Nitration of Polystyrene–Divinylbenzene Resin

Using the procedure given in "Preparation of Macroporous Resin", resin 1 has been prepared so that their average particles are large and have sizes lying

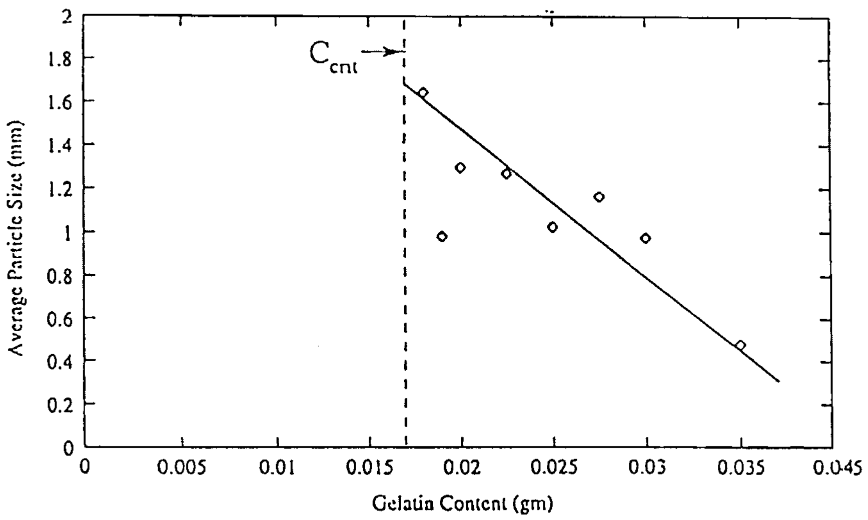


Figure 2. Effect of gelatin contents on particle size distribution of PS–DVB resin.

between 1 and 1.5 mm by keeping the amount of gelatin as 0.028 g in the recipe. Resins of uniform size are separated by sieving and are subjected to nitration. In order to accommodate a large amount of gas, we chose to work with a relatively large glass reactor (2.5 L) to accommodate the NO_x without increasing the reactor

Table 2. Change in Surface Area of Polystyrene Divinylbenzene (PS–DVB) Resin due to Modification

Type of Resin	Surface Area (m^2/g)
Unmodified PS–DVB resin	9.879
Nitrated PS–DVB resin	2.447
Aminated PS–DVB resin (1 hr)	2.539
Aminated PS–DVB resin (2 hr)	2.84
Aminated PS–DVB resin (3 hr)	2.861
Aminated PS–DVB resin (4 hr)	3.377
Aminated PS–DVB resin (5 hr)	3.594
Aminated PS–DVB resin (6 hr)	4.135
Aminated PS–DVB resin (7 hr)	6.297
Aminated PS–DVB resin (8 hr)	5.031
Aminated PS–DVB resin (9 hr)	4.938
Chlorinated form of anion exchanger from Dow Chemicals	1.243

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pressure significantly at the reaction temperature. The silicone rubber septum facilitates the introduction of a gas mixture with known amount of NO_x. To carry out the reaction smoothly a large oven was procured, which could accommodate at least six reaction vessels at a given time.

The effect of different reaction parameters upon the extent of surface nitration has been examined by varying the temperature, the amount of the gas fed, and the reaction time. For each set of reactions, the amount of consumed NO_x has been determined by adding 100 mL of distilled water to the reactor to dissolve the remaining NO_x followed by vigorous shaking. This converts the residual gas within the reaction into nitric acid (12). After this the polymer resin is separated, and the filtrate comprises HNO_3 solution, which is pale yellow in color. This solution is titrated with 0.1 N NaOH to determine the strength of HNO_3 in water, and the consumed NO_x is determined with the knowledge of the initial amount of NO_x introduced into the reaction bottle. The polymer resin is then washed, dried, and kept in a dessicator, and the nitrated resin 2 is found to have a change of color from white to golden yellow.

The reactions involving NO_x have been well studied in problems of pollution phenomena arising due to NO_x in atmosphere (15,16). The reactions are assumed to be triggered by nitrogen and the NO_2 produce O radical as follows:

$$NO_2 \xrightarrow{NO,\,N_2} NO + O^{\cdot} \tag{6}$$

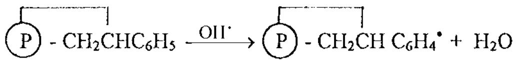
and these oxygen radicals react with moisture to give $OH^{\cdot}$ radical as follows:

$$H_2O + O^{\cdot} \leftrightharpoons 2OH^{\cdot} \tag{7a}$$

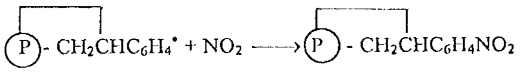
$$H_2O \leftrightharpoons OH^{\cdot} + H^{\cdot} \tag{7b}$$

These hydroxyl radicals are active species, which are assumed to give reactions involving NO_x. In a more recent study (17), the kinetics of formation of hydroxyl radical have been studied in the decomposition of peroxynitrous acid, and the first-order rate constants evaluated.

In our case, within the reactor, there is always air present in NO_x and reactions (6) and (7a,b) can always occur giving hydroxyl radicals within them. These radicals can abstract hydrogen from the resin, which can combine with NO_2 as shown below.



$$\text{(P)} - CH_2CHC_6H_5 \xrightarrow{OH^{\cdot}} \text{(P)} - CH_2CH\,C_6H_4^{\bullet} + H_2O \tag{8a}$$



$$\text{(P)} - CH_2CHC_6H_4^{\bullet} + NO_2 \longrightarrow \text{(P)} - CH_2CHC_6H_4NO_2 \tag{8b}$$

The FTIR Analysis of the Resin

Functional groups present in resins 1–3 after the reaction are determined instrumentally by FTIR (Perkin–Elmer 1600). The resin is first ground into fine powder and mixed with potassium bromide. The pellets of 1 cm size are prepared with the help of a hydraulic press, and samples of blank, nitrated, and aminated resins 1–3 have been used to determine FTIR spectra shown in Fig. 3. There are characteristic sharp peaks of NO_2 present at 700 and 1400 cm^{-1} for nitrated resin 2, which confirms the presence of NO_2 group. In resin 3, there is a strong absorption near 3100–3200 cm^{-1}, which confirms the presence of NH_2 group with simultaneous disappearance of peak at 1400 cm^{-1} belonging to NO_2.

Elemental Analysis Through Electron Spectroscopy for Chemical Analysis

For determining the binding energy of different elements present on the surface of PS–DVB resin, we carried out an ESCA analysis as described in "Bond Energy Determination Through ESCA", and the results are shown in Fig. 4. First, we examined the samples of resins 1, 2, and 3 for survey scan in the ranges 0–500 and 500–1000 eV. From this scan, individual elements (oxygen O 1s, nitrogen N 1s, and carbon C 1s) are scanned in their binding energy zones. After doing this, we prepared a scan in the range 275–325 eV for carbon, and a distinct peak of C 1s in Fig. 4a for carbon is observed at 284.2 eV in resin 1 as expected. Thereafter the nitrated resin 2 is scanned, and a peak at 295.3 eV for C 1s is observed. There is a shifting of 1.1 eV, which confirms the change in

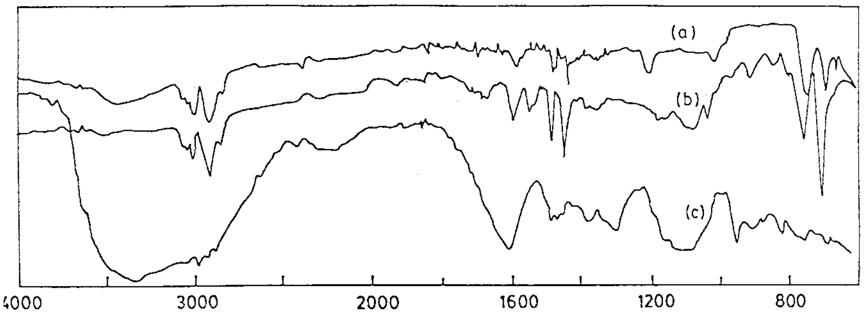


Figure 3. The FTIR analysis of (a) unmodified resin 1, (b) nitrated resin 2, and (c) aminated resin 3.

carbon binding. Again in resin 1, there is slight shifting in carbon C 1s peak position as shown in Fig. 4a. We then scanned nitrogen N 1s in the range of 400–450 eV for all these three samples. A characteristic peak of nitrogen at 407 eV is present in the nitrogen range 395–410 eV as shown in Fig. 4b. The scan of the PS–DVB resins show the nitrogen N 1s peak is at 450 eV and there is a decrease in the binding energy for aminated resin 3. This confirms the presence of a bond between the carbon and nitrogen and the NO_2 group is attached to the phenyl ring.

Determination of NO_x Consumed During the Reaction

The unreacted NO_x was determined by dissolving it in distilled water with vigorous shaking. The HNO_3, which is pale yellow in color, is titrated with 0.1 *N* NaOH to determine the strength of HNO_3 and by this way the amount of

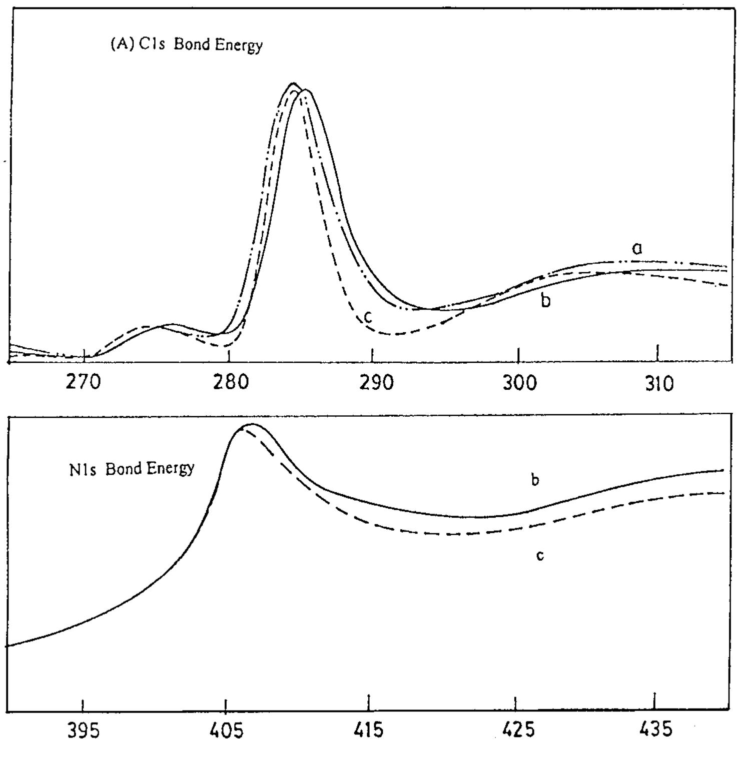


Figure 4. The ESCA analysis of (a) unmodified resin 1, (b) nitrated resin 2, and (c) aminated resin 3.

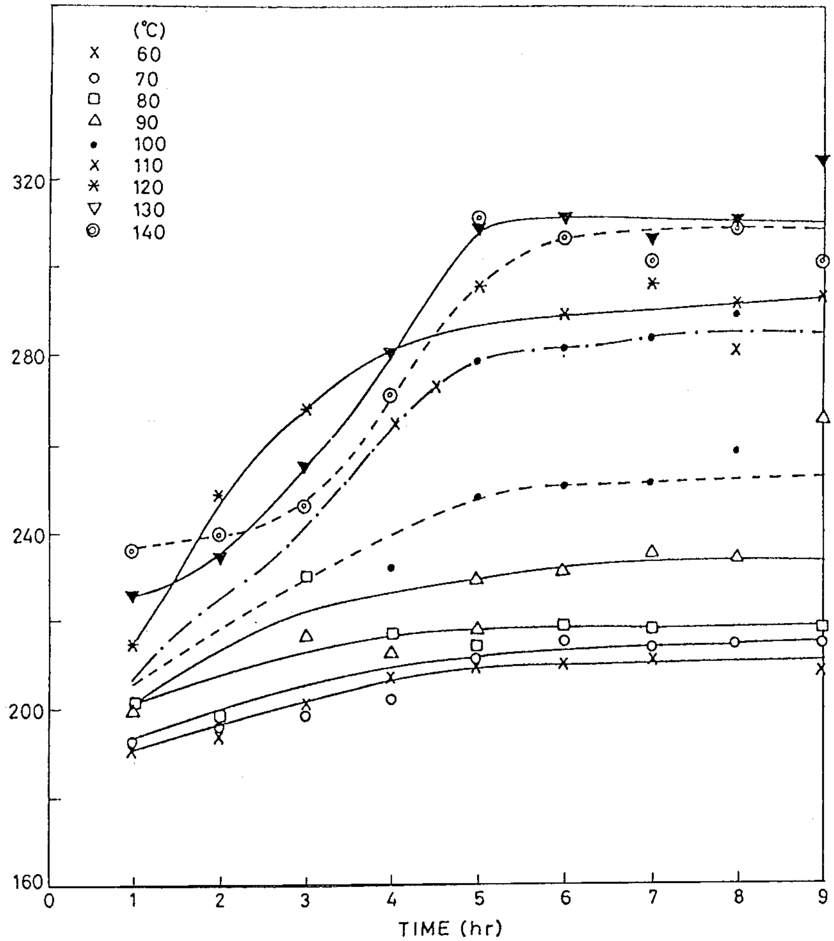


Figure 5. Effect of time and temperature on NO_x consumption during the nitration of resin 1.

consumed NO_x is determined. In this study, we have examined the NO_x consumption during the nitration reaction with time as well as temperature, and the results are shown in Fig. 5. It is observed that on increasing the time and temperature, the NO_x consumption first increases and then attains an asymptotic value for each temperature. At lower temperatures, the amount of NO_x reacting to the PS–DVB resin is less. However as we increase the temperature, the reaction rate increases and at 130°C the reaction of NO_x to the resin is maximum. We have

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already observed that at 140°C, the resin degrades and the fall in the NO_x consumption is because at this temperature, polymer degradation occurs, which changes its characteristics.

Effect of Temperature on the Exchange Capacity of Resin 3

It is expected that the extent of nitration reaction would increase with increasing temperature. Therefore, its effect on nitration of the resin is examined by varying the temperature at a step change of 10°C starting from 60 to 140°C. Beyond 140°C, resin 2 starts becoming brown in color and therefore we did not examine temperatures more than this. From Fig. 5, for 4 hr of nitration, it is observed that the maximum consumption of NO_x takes place at 130°C. Resin 2 formed at 130°C and 4 hr of reaction time was aminated to resin 3 and its exchange capacity determined. We observed that resin 3 cannot be regenerated using ASTM procedure and has only *one time* capacity. If resin 3 is converted to resin 6, it is found to become regenerable.

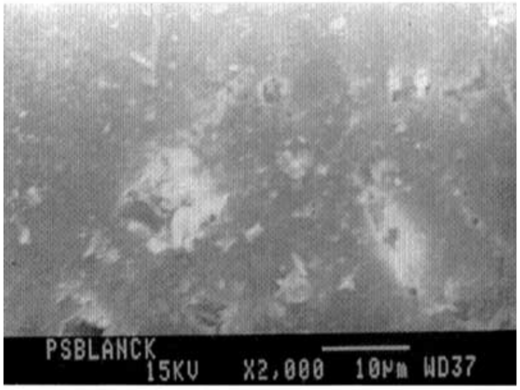
Effect of Modification on Morphology

To find out changes in the morphology of the surfaces due to modification reactions, we took scanning electron microscopy (SEM) photographs at 2000 × magnifications. These are shown in Fig. 6 for unmodified resin 1, after modification with NO_x and then after amination (or resins 1–3). From this figure, it appears that these chemical reactions in the polymer gel produce a morphological change over the surface. The aminated resin 3 carries crests over the surface at this modification, which are few in number, but are significant.

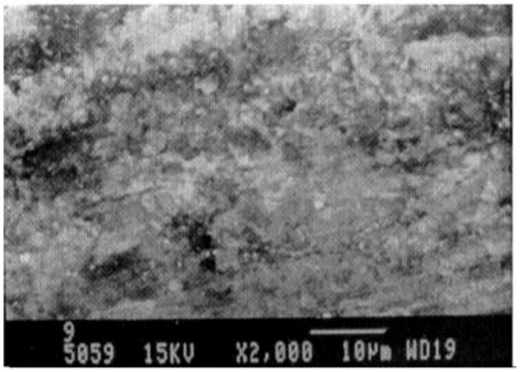
Effect of Modification on Surface Area

We determined the internal surface area of polymer particles using standard BET isotherms apparatus (Pulse Chemisorb 2700). We had already determined the surface area of unmodified resin earlier and now we report the effect on this by modified NO_x and aminated resins 2 and 3. The results are shown in Table 2 and we see no specific trend in these data. This is because on modification of the resin, its ability to retain moisture is increased considerably. We will be showing in "Equilibrium Water Content of Chloroethylated Anion Exchanger, Resin 6", that the moisture in these is held with greater solvation energy and is difficult to remove. For determination of surface area, the absorbed moisture of the sample may block pores and may give misleading results. It is desirable that the sample

(a) Unmodified Resin



(b) Surface Nitrated Resin



(c) Surface Aminated Resin

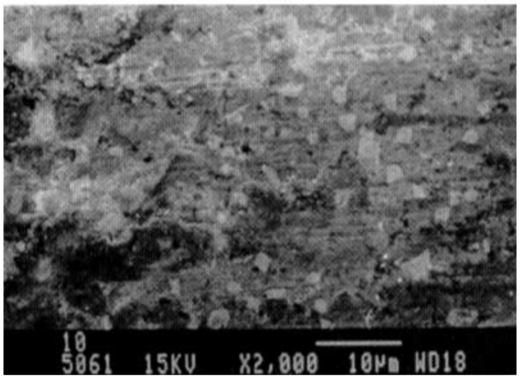


Figure 6. Effect of modification on surface morphology of PS–DVB resin 3.

should contain no moisture and should be completely dry, which we cannot accomplish completely and for this reason, the information on surface area in Table 2 could not be trusted.

Reproducibility of Experimental Data

In order to demonstrate the reproducibility of the experimental results, we carried out the gas phase nitration of PS–DVB resin at 130°C for various reaction times. The resultant nitrated resin 2 was aminated to form resin 3 and its one time exchange capacity determined. Since this aminated resin 3 cannot be regenerated, some of this was saved for further modification. As outlined in Eqs. (4a) and (4b), these were first reacted with dichloroethane to give resin 5 and then quaternized with the trimethylamine to give resin 6. The exchange capacity of these were determined and then subjected to regeneration cycles at least nine times. Experiments revealed that in the repeated experimentations the amount of NO_x consumed is reproducible to within 40% and that in the determination of exchange capacity, Q, is within 6%. As opposed to this, in the regeneration cycle Q is reproducible within 5%.

Exchange Capacity of Chloroethylated Resin 6

To study the effect of time on the nitration of PS–DVB resin, reaction was carried out for 9 hr and samples were taken out on an hourly basis. For this purpose, nine reactor bottles were put in the oven maintained at the desired temperature. One reactor bottle is withdrawn every hour, the reacted NO_x within the bottle is determined, and the results are plotted in Fig. 5. On increasing the reaction time, the color of the modified resin 1 changes gradually from white to pale yellow and brown to the naked eye. Now to examine the formation of nitrate groups in resin 2, it is converted to resin 3 and the capacity of the latter is determined. The one time exchange capacity results are plotted in Fig. 7. It is observed that on increasing the reaction time, the rate of nitration increases, thus the capacity of the modified resin 3 also increases and after 6–8 hr of reaction it reaches an asymptotic value. Experiments reveal that above 100°C, the capacity increases significantly and a prominent jump in capacity is visible clearly.

In order to make aminated resin 3 regenerable by standard ASTM procedure, it is modified to resin 6 [see Eqs. (4a) and (4b)]. In Fig. 8, we have examined the dependence of the exchange capacity of resin 6 with the duration of nitration carried out at 130°C. We observe a maximum exchange capacity of 4.8 meq/g of wet resin after 6 hr of nitration. Commercially available anion exchange resin is chloromethylated, its quaternized form has the structure of

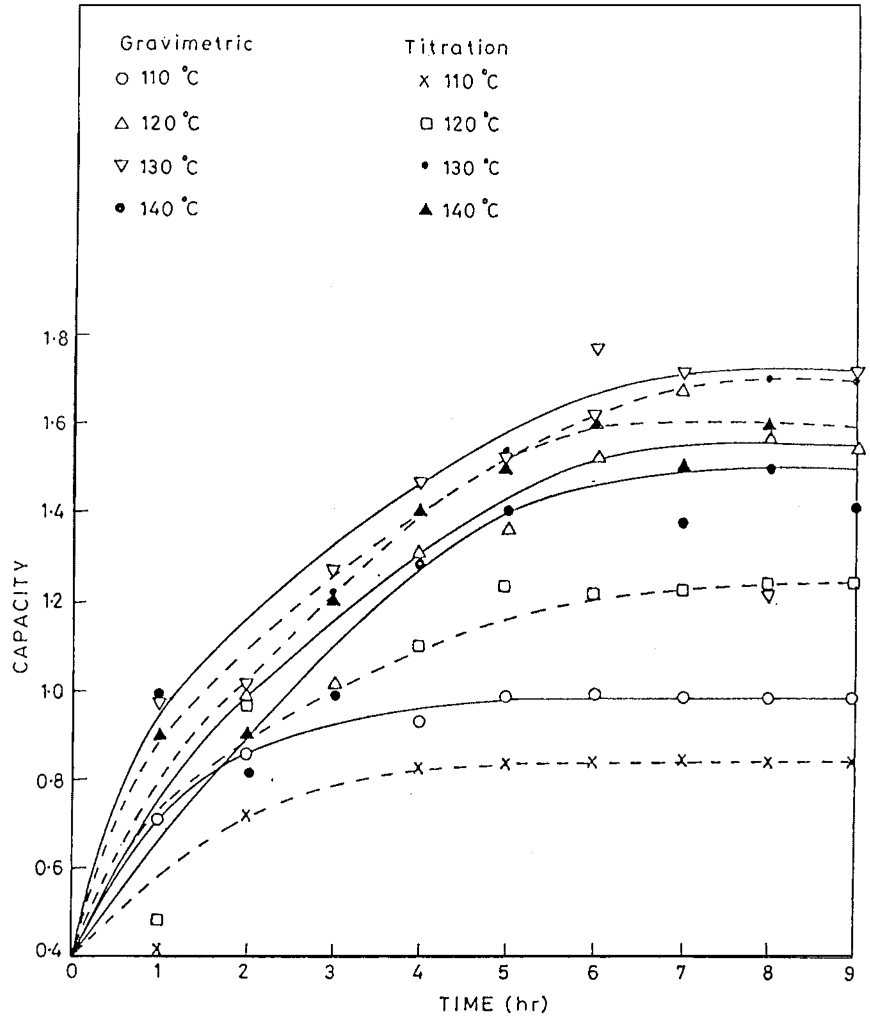


Figure 7. Effect of nitration time on the one time capacity of resin 3 for various temperatures.

Ⓟ– $CH_2CHC_6H_4CH_2N^+(CH_3)_3Cl^-$ and has the exchange capacity 1.68 meq/g of wet resin. Compared to this resin, resin 6 has a capacity of about three times the value.

It is recalled that 300 mL of NO_x or 13.39 mmol of NO_x was consumed completely per gram of the resin in the nitration reaction. If it is assumed that

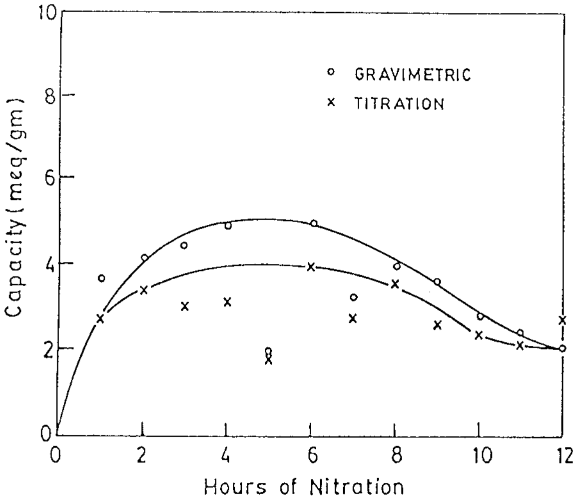


Figure 8. Effect of nitration time on the capacity of chloroethylated resin 6 that can be regenerated repeatedly by ASTM procedure. Capacity calculation is on the basis of wet gram of resin.

there is only one NH_2 group on the phenyl ring of resin 3, the anion exchanging group in resin 4 would be $NH_3^+Cl^-$. In resin 4, the molecular weight of the repeat unit $[-CH_2CH-C_6H_4NH_3^+Cl^-]$ would be 155.5 and would provide one exchangeable chloride ion. Let us assume N_o is the number of repeat units of polymer chain. Since resin 4 is a network, in the limit N_o should be infinity, however for real chains let us assume this to be some large number. For this ensemble of chains, its molecular weight is 155.5 N_o and it gives N_o exchangeable chloride groups. In other words, on a dry basis, it should give a capacity of $N_o/(155.5\,N_o)$ or 6.39 meq/g of dry resin, a value that is independent of chain length. We have already observed that 13.39 mmol of NO_x is completely reacted to each gram of the resin and in Fig. 7 we have observed the maximum capacity reached is 4.8 meq/g of wet resin. In a later section ("Equilibrium Water Content of Chloroethylated Anion Exchanger, Resin 6"), we have shown that the equilibrium moisture content of resin is 69%, which means that on a dry basis, the capacity would be 4.8/0.31 or 15.5 meq/g of dry resin, which satisfies the material balance approximately. In addition, this also suggests that a capacity of 15.5 meq/g of dry resin can be explained only by multiple nitration of a given repeat unit (or at best two nitration groups giving a maximum of four sites). Secondly, the resin reported in this work has low surface area with less than 1% of phenyl rings on the surface of internal pores. This suggests that most of the

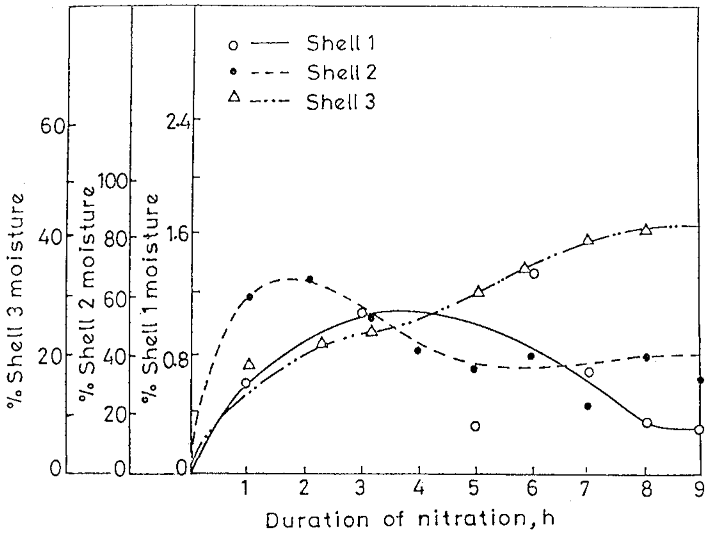


Figure 9. Percent moisture content of chloroethylated strong base resin 6. The basis for moisture calculation is the mass of dry resin.

modification reactions must have occurred within the polymer gel phase with negligible reaction on the surface.

Determination of Rate Constant

In the process of modification of PS–DVB resins, we carried out their gas phase nitration as the first step, followed by their amination. We have already discussed the reaction chemistry in "Nitration of Polystyrene–Divinylbenzene Resin", and using NO_x conversion data, we now desire to determine the kinetics of the nitration reaction. Experimental results show that the NO_x intake during the nitration reaction increases asymptotically as the time of nitration increases.

In the previous section, we have shown that the nitration of polymer chains in resin 2 occurs within the gel medium. This means that according to basic mechanisms given in Eqs. (8a) and (8b), the hydroxyl radicals must be generated in the gas phase and then diffuse into the polymer gel along with molecules of NO_x. This suggests that the overall nitration reaction in "Nitration of Polystyrene–Divinylbenzene Resin" is a multiple step process and its mathematical analysis would be complex. In the Appendix, we have assumed first-, second-, and third-order kinetics for the gas phase consumption of $[NO_x]$ vs. t data as well as capacity Q vs. t data and carried out a linear regressional analysis using $y_{,\text{model}} = ax_{\text{I}} + b$ type equation. Since at $t = 0$, conversion of NO_x as well as Q is strictly zero, b in this relation is identically equal to zero. We have computed (18)

$$S_r = \sum_{i=1}^{n} (y_i - y_{i,\text{model}})^2 \tag{9a}$$

$$S_t = \sum_{i=1}^{n} (y_i - \bar{y})^2 \tag{9b}$$

$$\bar{y} = \frac{1}{n}\sum_{i=1}^{n} y_i \tag{9c}$$

and $S_t > S_r$ implied that there is clustering of data and $y = \bar{y}$ is a better representation of data compared to a line passing through the origin. The regressional analysis shows that in the first-order kinetic model there is clustering and by increasing the order to the second- and third-order kinetic model, the fit of the data improves considerably as seen from the values of coefficient of correlation r. We find the reverse trend when we start fitting the capacity Q vs. t data. On increasing the order of the kinetic model, the coefficient of correlation r falls. Since we have already found that all NO_x molecules show up as nitrate groups in resin 2, it is expected that the kinetic order of both conversion of NO_x vs. t and Q vs. t should have the same order. This means that the regression analysis suggests the second-order kinetic model.

Equilibrium Water Content of Chloroethylated Anion Exchanger, Resin 6

Ion exchangers (1,4) usually absorb water and swell due to their solvation ability. This swelling occurs up to a point where an equilibrium is attained. We followed the experimental procedure given below to determine this and to assess the solvation ability of resin 6 prepared in this paper.

(a) *Saturation of polymer resin with moisture*. Approximately 1.5 g of resin, which has already been dried in dessicator for at least 6 months is weighed and placed in a standard joint conical flask. This resin is refluxed with 100 mL of distilled water for 4 hr. The resin is separated and dried of the water adhering to it with the help of filter papers.

(b) *Oven drying*. The surface dried resin is once again weighed, which is a wet mass of the resin. In order to assess how strongly water is solvated by resin 6, we have carried out drying in two stages. In the first one, the resins are placed in an oven maintained at 105 ± 2°C for 4 hr and weight is determined after this. The mass of water lost by this procedure is called Shell 1 moisture.

(c) *Vacuum drying*. In the second stage of drying, the resin from the oven is subjected to vacuum drying at 100°C for 24 hr at 750 mmHg vacuum. The mass of moisture lost by this procedure has been termed Shell 2 moisture.

(d) *Vacuum drying for 6 months at ambient temperature under* P_2O_5. The resin obtained from stage 2 drying is stored in a vacuum desiccator for 6 months. The moisture lost this way has been called Shell 3 moisture.

The first two stages of drying have been chosen such that commercial chloromethylated resin loses moisture completely. The unmodified resin loses the absorbed water completely after first stage of drying while the commercial chloride form, strong base anion exchange resins from Dow Chemicals (obtained by chloromethylation) lose 11.4% absorbed water after the first stage while the remaining 32.13% is lost by second stage drying.

The results for Shell 1–3 moistures for resin 6 have been plotted in Fig. 9 as a function of duration of nitration. We observe that Shell 1 and 2 moistures first rise with nitration time, but after about 5 hr they fall to reach an asymptotic value for larger reaction times. However, Shell 3 moisture continues to rise eventually reaching an asymptotic value. Coincidentally the time where Shell 1 and 2 moistures fall is also the time when the maxima in exchange capacity occur and the total moisture content is about 69% independent of the nitration time.

CONCLUSIONS

In this paper, we have developed a clean technology for nitration of PS–DVB resin. The consumption of NO_x has been determined by dissolving unreacted gas in water and the analysis of capacity of resin 6 shows that every molecule of NO_x reacted shows as an amine group in the resin. In addition, we have shown that the high capacity of the resin can arise only when there is more than one exchanging site on every repeat unit of the polymer. On carrying out the regressional analysis of kinetic data of consumption of NO_x and capacity vs. time, the assumption of the second-order kinetics gives the best results.

We have investigated the effect of duration of nitration upon the exchange capacity of anion exchanger, resin 6. We have found that for short duration, the exchange capacity rises, which falls slightly for larger times. In order to assess the solvation ability of the chloroethylated resin prepared in this work, we devised three stages of drying, which give Shell 1–3 moistures. Shell 1 and 2 moistures are the ones that are held by corresponding chloromethylated resin in the same mass. For chloroethylated resin, Shell 1 and 2 moistures rise for short nitration times, however they fall after about 5 hr of nitration to take on a lower asymptotic value. The Shell 3 moisture continues to rise indicating that the solvation ability of this resin increases with the duration of nitration and is likely to be responsible for the high exchange capacity observed.

APPENDIX

Linear Regression Analysis of Experimental Data of NO_x Consumption vs. Time and Data on Exchange Capacity of Resin 3 vs. Time

For the data of conversion of NO_x vs. time, we desire to determine the order n of the reaction in the following.

$$\frac{\mathrm{d}C_A}{\mathrm{d}t} = kC_A^n$$

We now examine the first-, second-, and third-order kinetics (or $n = 1$, 2, and 3) and integrate the above equation to obtain the following. We then carried out the regressional analysis of the data of consumption of NO_x vs. time to determine the rate constants at the different temperatures. We determined their temperature dependence subsequently by another regressional analysis and report the results below for every model.

(1) Gas Model 1 ($n = 1$)

$$-\ln(1 - X_A) = k_1 t$$

Best fit rate constant $k_1 = 0.67 \exp(-478.82/T)$

(2) Gas Model 2 (for $n = 2$)

$$\frac{X_A}{1 - X_A} = k_2 C_{A_o} t$$

Best fit rate constant $k_2 = 4.65 \times 10^2 \exp(-692.09/T)$

(3) Gas Model 3 (for $n = 3$)

$$\frac{2X_A - X_A^2}{(1 - X_A)^2} = 2k_3 C_{A_o}^2 t$$

Best fit rate constant $k_3 = 2.899 \times 10^4 \exp(-813.65/T)$

Above X_A is the conversion of NO_x which is strictly zero at $t = 0$. This implies that in the regression line $A_o = 0$ and the number of data points that we have taken is 10.

The analysis of experimental data of NO_x conversion vs. t has been carried out for different gas models. For the first-order model, variable S_r is less than S_t which means that data to clustering around mean gives less total error. Thus, we conclude that the assumption of first-order kinetics is a poor one. The assumption of second-order kinetics shows that for four out of nine temperatures studied, $S_r > S_t$. As opposed to this for $n = 3$, such a condition does not arise and correlation coefficient for the data is above 60%.

For solid phase kinetic studies for exchange capacity, Q vs. t data, we assume that every molecule of NO_x reacted shows up as an NH_2 group within the resin. In view of this, the integrated 1st, 2nd, and 3rd kinetic model can be written by replacing X_{NO_x} with Q/Q_∞ to obtain in earlier relations would be given

(1) Solid Model 1

$$-\ln\left(1 - \frac{Q}{Q_\infty}\right) = k_1 t$$

Best fit rate constant $k_{Q1} = 0.061\exp\{-734.46/T\}$

(2) Solid Model 2

$$\frac{Q/Q_\infty}{1 - Q/Q_\infty} = k_2 Q_\infty t$$

Best fit rate constant $k_{Q2} = 9 \times 10^{-3}\exp\{-766.00/T\}$

(3) Solid Model 3

$$\frac{(Q/Q_\infty)(2 - Q/Q_\infty)}{(1 - Q/Q_\infty)^2} = 2k_3 Q_\infty^2 t$$

Best fit rate constant $k_{Q3} = 3.84 \times 10^{-4}\exp\{-1.38 \times 10^4/T)$

Here Q_∞ is the asymptotic exchange capacity (at $t = \infty$).

The experimental data on exchange capacity Q has been analyzed for different kinetic models. A careful examination of results reveals that in these $S_t > S_r$ which implies that it is possible to determine best line passing through origin. However, for first-order solid model 1, except for $T = 120°C$, the correlation coefficient r was above 75%. As the kinetic order n increases, results show that the fit becomes poorer. The second-order fit for both these data appear to give optimal results. The regression analysis data yield rate constants, which are given along with the models given above.

REFERENCES

1. Kumar, A.; Gupta, R. *Fundamental of Polymers*; McGraw-Hill: New York, 1998.
2. Akelah, A.; Moet, A. *Functionalized Polymers and Their Applications*; Chapman and Hall: London, 1990.
3. Hodge, P.; Sherrington, D.C. *Polymer Supported Reaction in Organic Synthesis*; John Wiley: New York, 1980.
4. Helfferich, F. *Ion Exchange*, 1st Ed.; McGraw-Hill: New York, 1962.
5. Streat, M. *Ion Exchange for Industry*, 1st Ed.; Ellis Harwood: Chichester, 1988.
6. Pepper, K.W.; Paisley, H.M.; Young, M.A. Properties of Ion-Exchange Resins in Relation to Their Structure. Part VI. Anion-Exchange Resins Derived from Styrene–Divinyl Benzene Copolymers. J. Chem. Soc. **1953**, 4097–4105.
7. Balakrishnan, T.; Ford, W.T. Particle Size Control in Suspension Copolymerization of Styrene, Chloromethyl Styrene and Divinylbenzene. J. Appl. Polym. Sci. **1982**, *27*, 133–138.
8. Lewandowski, K.; Svec, F.; Frechet, M.J.J. Preparation of Macroporous, Nonodispersed, Functionalized Styrene–Divinylbenzene Copolymer Beads: Effect of the Nature of the Monomers and Total Porogen Volume on the Porous Properties. J. Appl. Polym. Sci. **1992**, *67*, 2443–2449.
9. Egawa, H.; Nonaka, T.; Nakayama, M. Influence of Crosslinking and Porosity of Uranium Adsorption of Macroreticular Chelating Resin Containing Amidoxin Groups. J. Macromol. Sci. Chem. **1988**, *A25*, 1407–1415.
10. Upadhye, A.S. Study of Aging of Joints in PMMA Beans Using Impact Response. M.Tech. Thesis, Department of Chemical Engineering, Indian Institute of Technology, Kanpur, India, 1996.
11. Awasthi, V.K. Development of Repair Technology for Glass Epoxy Composites by Surface Modification M.Tech. Thesis, Department of Chemical Engineering, Indian Institute of Technology, Kanpur, India, 1997.
12. Vogel, A.I. *Text Book of Macro and Semi Macro Qualitative Inorganic Analysis*; 1953, 338–340.
13. Cotton, F.A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th Ed.; John Wiley and Sons: New York, 1992; 320–325.
14. IS, *7330–1988, Indian Standard Method of Sampling and Test for Ion-Exchange Resins (First Revision)*; and ASTM No. ASTMD 2187, 2687, 3087 and 3375 Bureau of Indian Standard: New Delhi, 1989.
15. Wayne, R.P. *Chemistry of Atmosphere*, 2nd Ed.; Clarendan Press: Oxford, 1991.

16. Warneck, P. *Chemistry of the Natural Atmosphere*, 1st Ed.; Academic Press: San Diego, 1988.
17. Coddington, J.W.; Hurst, J.K.; Lymar, S.V. Hydroxyl Radical Formation During Peroxynitrous Acid Decomposition. J. Am. Chem. Soc. **1999**, *121*, 2438–2443.
18. Chapra, S.C.; Canale, R.P. *Numerical Methods for Engineers*, 2nd Ed.; McGraw-Hill: New York, 1989.

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