

Effect of Chemical Modifications upon Exchange Capacity of Aminated Macroporous Styrene–Divinyl Benzene (PS–DVB) Copolymer Anion Exchange Resin

NAMITA JAYASWAL, SHISHIR SINHA, ANIL KUMAR

Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, 208, 016, India

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ABSTRACT: The macroporous PS–DVB resin was prepared in the laboratory by suspension polymerization using gelatin as stabilizer and toluene as porogen. This is subsequently nitrated by a mixture of NO and NO₂ (called NO_x) in a gas phase reaction, and the carbon–nitrogen covalent bonding has been demonstrated by modified Laissagne spot test, FTIR, and ESCA analysis. This has been aminated by reducing the nitrate groups using hydrazine hydrate, and the resultant weak base anion exchange resin was shown to have a one-time exchange property because of its inability to be regenerated by the usual ASTM procedures. The chloroethylated PS–DVB resin is prepared by reacting aminated resin with dichloroethane, and is shown that two molecules of the latter react with every amine group. The regenerable strong-base anion exchange resin is then prepared by quarternizing it with tertiary (trimethyl and triethyl) amines and triphenyl phosphine, and it is shown that these gegen ions have a considerable effect on the exchange ability of the resin. We have found the duration of nitration to be the most important parameter affecting the capacity, and in this work, we report studies for all these gegen ions. It is found that for any gegen ion, the exchange capacity first increases for short times of nitration, reaches a broad maxima of around 5 mEq/g of wet resin with about 69% moisture content (or 15.48 mEq/dry g), and falls slightly for larger times of nitration due to a slight degradation. This is to be compared with commercial chloromethylated resin, which has an exchange capacity of 1.68 mEq/g of wet resin with 43.53% moisture content (or 2.97 mEq/dry g of resin). It is found that the resin with triphenyl phosphine as a gegen ion gives the highest exchange capacity, while the one with trimethyl gives the lowest. To assess the solvation ability of the chloroethylated resin prepared in this work, we evolved three stages of drying consistent with the literature such that in the first stage, unmodified resin loses moisture completely (shell 1 moisture), in the second stage, chloromethylated (commercial anion exchange) resin loses moisture completely (shell 2 moisture), and in the third stage chloroethylated resin loses moisture completely (shell 3 moisture). With the increase in the duration of nitration, the shell 1 and 2 moistures first increase, but after 5 h of nitration they fall to lower asymptotic values for a large duration of nitration. However, shell 3 moisture keeps on increasing and is the highest for triphenyl phosphine gegen ion and the lowest for trimethyl amine. This increased solvation ability of chloroethylated resin is likely to be responsible for higher exchange ability of the resin reported in this work. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1735–1748, 2001

Key words: chemical modifications; surface-aminated macroporous styrene–divinyl benzene; anion exchange resin

INTRODUCTION

Exchangers are insoluble solid material that carry either chelating functional groups, cations,

or anions or all three of them. Among all these, the most important are organic exchangers, which are crosslinked polymer gels.^{1–5} The properties of these arise because of the functional groups in it, and these are created on the polymer gel by modification techniques. Commercially, the organic material most commonly used is a copoly-

Correspondence to: A. Kumar.

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mer gel of styrene and divinylbenzene (denoted by PS-DVB) and the general purpose resin contains about 8–25% of the latter. This is because, this resin has preponderance of phenyl rings that can be easily functionalized. All functionalizing reactions in the literature reported are found to be liquid phase reactions in which penetration of reagents into the resin is extremely important and is usually small. The common starting point of these reactions is invariably the chloromethylation in which chloromethyl ($-\text{CH}_2\text{Cl}$) groups are generated on phenyl rings using an extremely carcinogenic reagent chloromethyl methyl ether (CMME). The overall reaction is not efficient, and about 4–6% chloromethyl groups per gram of resin is all that can be obtained and the unreacted CMME rejected.

In this article we report a gas phase nitration of macroporous PS-DVB copolymer resin, using a mixture of NO and NO_2 gas (sometimes called NO_x) at relatively low temperatures, which has not been reported in literature. For the purpose of anion exchange resins, aminated resin can be easily prepared by reducing these nitrate functional groups with hydrazine hydrate. The chloroethylated resin is prepared by reacting with dichloroethane and the exchange resins formed by quaternizing it with tertiary amines or phosphines. We have found the duration of nitration and the nature of gegen ion as important two variables affecting the exchange capacity of this resin, and we report their effects here. It was found that the exchange capacity of our resins on a dry basis to be about five times more compared to that of commercial anion exchange resins.

EXPERIMENTAL

Preparation of Macroporous Resin

To get large particles of PS-DVB copolymer resin, the technique of suspension polymerization has been used.^{6–9} In this study the organic phase is prepared by mixing styrene (280 g 3.04 g-mol), divinylbenzene (80 g 0.62 mol), azobis-isobutyronitrile (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 $60 \pm 2^\circ\text{C}$ for 4 h in a setup shown in Figure 1. After this time, the temperature of the reaction mass is increased

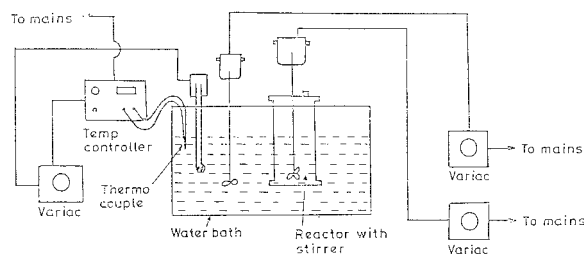


Figure 1 Experimental setup for preparation of R_1 resin.

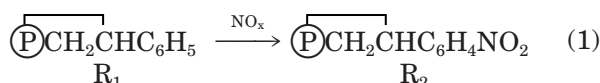
to $90 \pm 2^\circ\text{C}$ in half an hour, and then it is kept constant for the next 2 h. These resins now have considerable mechanical strength, and are separated and washed with water. To remove excess calcium carbonate, 0.1 N HCl solution is added to the resin. Again, the resin is separated, washed with water and finally with methanol, and is then dried in an oven maintained at $70\text{--}75^\circ\text{C}$. During experimentation, gelatin content in the aqueous phase is found to play an important role in controlling the particle size of the resin, and it is found that the average particle size tends to decrease with the increase in gelatin content.

Gas Phase Nitration of PS-DVB Resins using NO_x

Direct gas phase nitration of polystyrene-divinylbenzene (PS-DVB) resin occurs extremely efficiently in the presence of small amounts of NO, and is carried out in a 2.5-liter reaction bottle. This reaction vessel is equipped with an aluminium 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-liter, two-neck round-bottom flask by reacting sodium nitrite NaNO_2 (10 g, 0.15 mol) with sulfuric acid (H_2SO_4 sp.gr.1.18, 25 mL) in the presence of ferrous sulfate FeSO_4 (5 g, 0.03 mol). The flask is equipped with a rubber septum for withdrawing NO_x , and the gas is withdrawn with the help of a 100-mL syringe.

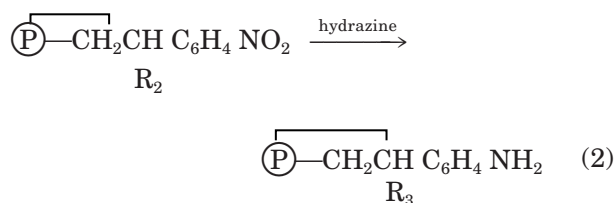
Approximately 1.5 g of PS-DVB resins are introduced into the reaction vessel and are placed in an oven maintained at the desired reaction temperature. A small needle is punctured through the silicon septum of the reactor vessel so as to allow a thermal equilibrium with the oven. The gas inside the bottle 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 a 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 an 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 one repeat unit of the unmodified resin is represented by R_1 , the overall nitration reaction process can be schematically written as:



Amination of Nitrated R_2 Resin

Amination of the nitrated R_2 resin is carried out with hydrazine hydrate as follows: 1.5 g of R_2 resin is placed in a conical flask with 50 mL of hydrazine hydrate and the reaction mass is refluxed at 60°C for 4 h in an oil bath maintained at about 60°C. After refluxing is over, the resin is filtered, then properly washed with distilled water and dried. These aminated R_3 resin is formed through following reaction and is ready for further processing.



The capacity of these resins is determined through the procedures given below:

Determination of Capacity

We have determined the exchange capacity of anion exchange resins by the two procedures given here. The titration procedure is simpler, and is easier to carry out, while the gravimetric procedure is the standard ASTM recommended method. On the comparison of these two techniques the titration method has larger scatter in data and invariably underestimates the capacity results.

Titration Method

This method is based on the fact that all amine groups would react with HCl to give a quarternized ammonium salt. In view of this, the procedure consists of placing approximately 1.5 g of R_3 resin in a conical flask and refluxing it with 50 mL of 0.1 N HCl for 4 h. The reaction mass is then filtered, and the filtrate contains unconsumed HCl, which is titrated with 0.1 N NaOH to determine the chlorine ion intake by the aminated R_3 resins. The titration is carried out using a phenolphthalein indicator (1% solution in ethanol). Again, the carefully washed and dried aminated resins are refluxed with 0.1 N NaOH for 4 h. The concentration of the remainder NaOH is determined by titration with 0.1 N HCl using a phenolphthalein indicator and the capacity of R_3 resin is calculated. This always gives a lower value compared to the gravimetric method.

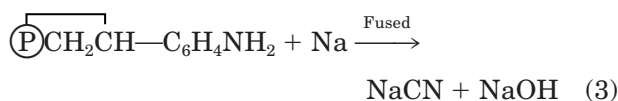
Gravimetric Method

The method of determining exchange capacity of resin given in ASTM standard No. ASTM D 2187, 2687, 3087, 3375) is the gravimetric method consisting of 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 the R_3 resin in a quantity of 100 mL per gram and kept for 24 h. After this, the resin is filtered and washed with distilled water until 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 resin that is free from the mixed acid. (b) Determination of capacity: the regenerated resin obtained from the 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 h. 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 h. The chlorine ion present in the filtrate form AgCl , which is precipitated. This precipitate is filtered and weighed, and the capacity of the aminated resin is calculated.

Elemental Test for Nitrogen Detection in R_3 Resin^{12,13}

To detect nitrogen over the R_3 resin, the Lassaigne element spot detection test has been

slightly modified. In this element nitrogen detection test, the polymer resin is fused with metallic sodium to form sodium cyanide as follows:



The entire content is then washed with water and 2–3 mL of this filtrate solution is poured into a test tube containing 0.1–0.2 g of powdered iron (II) sulphate crystals. The mixture is then heated gently with shaking, then without cooling, dilute sulfuric acid is added to dissolve the metallic hydroxides and the Prussian blue color of the mixture formed confirms the presence of nitrogen.

Bond Energy Determination through Electron Spectroscopy for Chemical Analysis (ESCA)

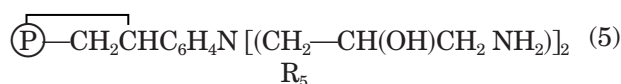
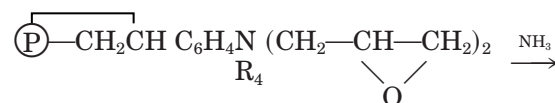
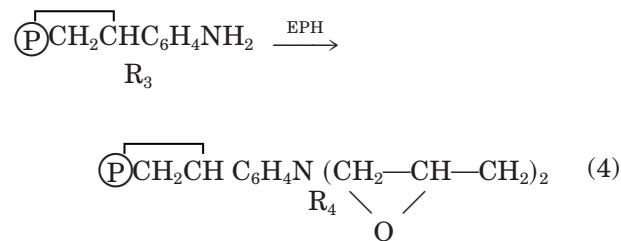
In this technique the resin is bombarded with particles of high energy like electrons, photons, and ions. Quantitative/qualitative elemental information can be deduced from the ESCA by determining the specific bond energies for elements. Incident photons are generated from aluminium and are bombarded on solid R_1 to R_3 resins. This generates inner shell electrons known as photoelectrons and their kinetic energy distribution from which the binding energies are calculated. This technique is a one level transition process and gives chemical states of elements on the surface by measuring the chemical shifts in addition to the elemental detection capability.

The instrument used in this study is ESCA VG MK.II by VG Scientific, UK. For determining the binding energy of different elements presents in the resins, the sample is first baked for 8–10 h at 170–200°C. This operation is performed for obtaining the clean surface, and is necessary whenever the vacuum is broken or changed. After proper baking, the sample is introduced to a sample holding track/tray in the main chamber by a sample transport mechanism. Our samples are in the form of a 1 mm size, and the vacuum inside the system is maintained at 10^{-9} mmHg. The survey scan is taken in the two regions of 0–500 eV 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. After this information and the information available from standard samples, each element is individually scanned for different binding energy range. 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, to analyze the binding energy of a particular element and its shifting from its standard value, a sample depth scan is taken individually for carbon in the range of 275–325 eV, for oxygen in the range of 525–575 eV, and for nitrogen in the range of 400–450 eV. After getting the depth scan, peaks shifting from standard elements are calculated and thereby analyzed for the bond energy to distinguish the exact bonding and bond position of various functional groups (NO_2 and NH_2 in this case) positioned on the resins.

Modification of Aminated R_3 Resin with Epichlorohydrin

The aminated R_3 resin is refluxed with 50 mL of 5% v/v of epichlorohydrin (EPH) in ethanol for 4 h. The resin is then filtered, washed, and dried. The dried resin is then reacted with ammonia water to get amine groups, and in this step there is significant change in color due to modification with epichlorohydrin, as shown in Figure 2. The reactions occurring are as follows:



Modification of Aminated PS–DVB Beads with Dichloroethane

Approximately 1.5 g of R_3 resin is refluxed with 50 mL 2% v/v solution of dichloroethane in ethanol for 4 h. After the completion of the reaction-

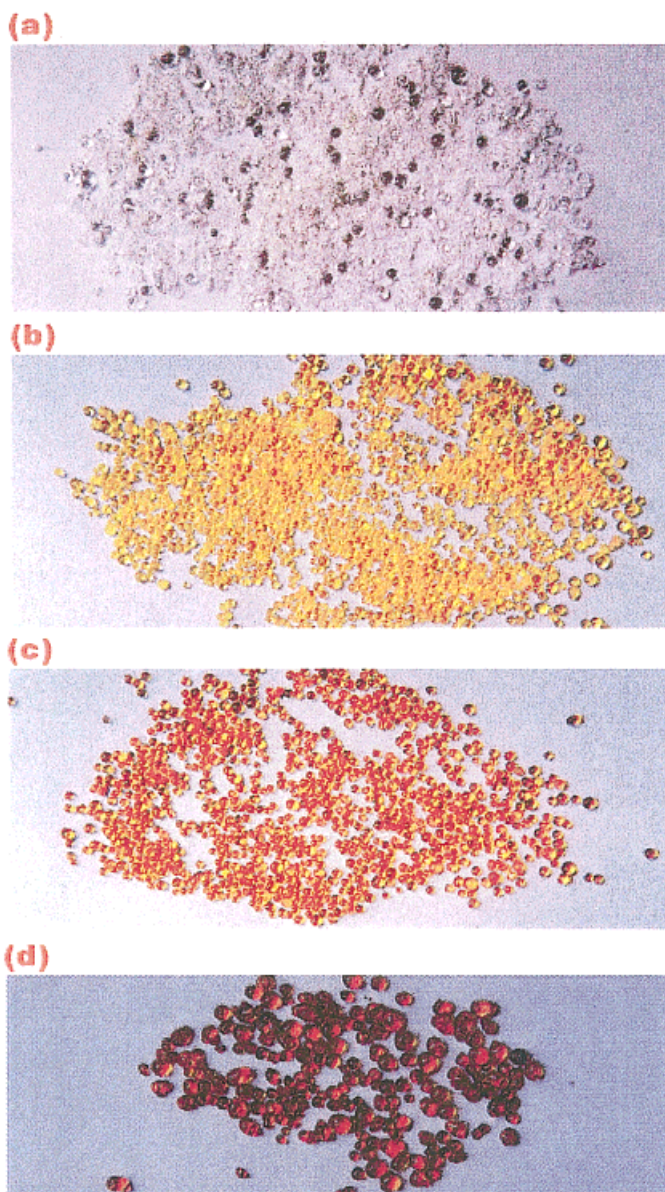
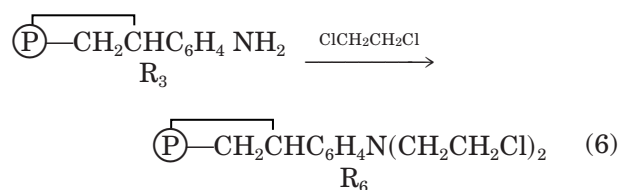


Figure 2 Effect of modification on color of PS-DVB resin: (a) unmodified, (b) nitrated R_2 resin, (c) aminated R_3 resin, (d) epichlorohydrin reacted R_5 resin.

,the resin is filtered, washed, and dried. Higher concentrations of dichloroethane are avoided because the resin becomes sticky and lumps are formed. No visible change in color is observed, and the reaction occurred as follows:



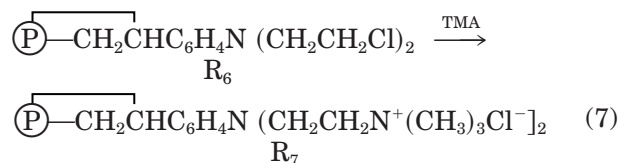
Now this R_6 resin can be easily quarternized with trimethylamine (TMA), triethylamine (TEA), and triphenyl phosphine (TPP) as described below.

Modification of Chloroethylated-Treated R_6 , with Trimethylamine, Triethylamine, and Triphenylphosphine

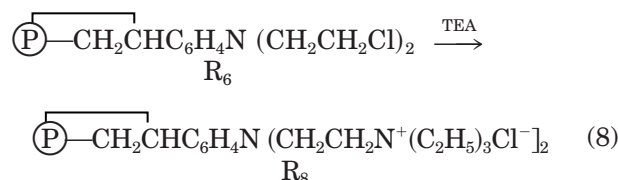
After modification with dichloroethane, the dried R_6 resin is treated with 20 mL of 5% v/v trimethylamine in ethanol, and the entire content is refluxed for 4 h. In an another set saturated solution of triphenylphosphine is prepared in ethanol and 20 mL of this saturated solution is refluxed

with 1.5 g of modified R₆ resin for 4 h. After the completion of the reaction, the resin is washed and dried, and is ready for examining the anion exchange capability. The reaction occurring during the above treatment can be written as:

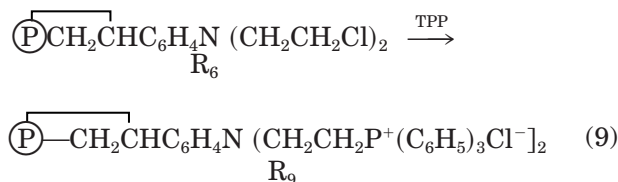
(i) Reaction with trimethylamine (TMA):



(ii) Reaction with triethylamine (TEA):



(iii) Reaction with triphenylphosphine (TPP):



The R₇ to R₉ resins are examined for functional group attachment in the resin, and their anion exchange capacity by procedures described earlier.

Determination of Equilibrium Water Content

Ion exchangers^{1,4} usually absorb water and swell due to their solvation ability. This swelling occurs up to an extent that an equilibrium is attained. Based upon the experimental procedure given in refs 1 and 4, we introduced one more intermediate drying stage to determine this, and assess the solvation ability of the R₇ to R₉ resin prepared in this work. Commercial chloromethylated resins are completely dehydrated in stage (c) of drying below.

- (a) Saturation of Polymer Resin with Moisture: approximately 1.5 g of resin, which has already been dried in dessicator for 6 months is weighed and placed in a standard joint conical flask. This resin is refluxed with 100 mL of distilled water for 4 h. It is separated and dried from water adhering to it with the help of filter papers.
- (b) Oven Drying: the surface-dried resin is once again weighed, which is the wet mass of the resin. To assess how strongly water is solvated by the resin, we have carried out drying in two stages. In the first one, the resin is placed in an oven maintained at 105 ± 2°C for 4 h and the weight is determined after this. The mass of water lost by this procedure is called Shell 1 moisture.
- (c) Vacuum Drying for 24 h: in the second stage of drying, the resin from the oven is subjected to vacuum drying at 100°C for 24 h at 750 mmHg vacuum. The mass of the moisture lost by this procedure has been termed as Shell 2 moisture.
- (d) Vacuum drying for 6 months at ambient temperature under P₂O₅: the resin obtained from stage 2 drying is stored in a vacuum dessicator for 6 months. The moisture lost this way has been called as Shell 3 moisture.

The first two stages of drying have been chosen so that commercial resin loses moisture completely in step (c). The unmodified resin loses the absorbed water completely after the first stage of drying, while the commercial Dowex strong-base anion exchange resins (obtained by chloromethylation) lose 11.40% absorbed water after the first stage while the remaining 32.13% is lost in stage (c) drying. This gives a total moisture of 43.83%, which compares well with its ratings of 36–42% for the Dowex resin from Dow Chemicals.

RESULTS AND DISCUSSION

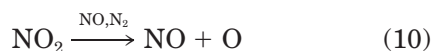
The study of this article is divided into eight sections dealing with (a) formation of aminated resin, (b) chemical characterization of various functional groups, (c) effect of modification on surface area and morphology, (d) further modification of aminated resin, and (e) solvent effect on modification. These are discussed below.

Nitration of Polystyrene–Divinylbenzene Resins

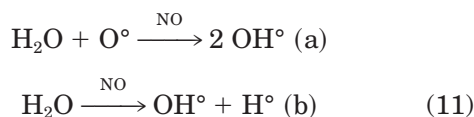
Using the procedure given earlier, the PS–DVB copolymer resins have been prepared so that their

average particles are large and have sizes lying between 1 to 1.5 mm by keeping the amount of gelatin as 0.028 g in the recipe. The beads of uniform size are separated by sieving, and these are subjected to nitration and have the surface area of 8.9 m²/g of the resin. To accommodate large amounts of gas, we chose to work with a relatively larger glass reactor (2.5 liters) to accommodate the NO_x without significantly increasing the reactor pressure at the reaction temperature. After the reaction is over, the bottle is washed with distilled water and the resin separated. The nitrated resin is found to undergo a change in color, as seen in Figure 2 from white to golden yellow. The nitrated resin was subjected to the modified Laissagne test, described in the Experimental section, which showed positive, this way confirming the C—N bond formation.

The reactions involving NO_x has 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 NO₂, which produce an O radical as follows



and these oxygen radicals react with moisture to give an OH° radical as follows



These hydroxyl radicals are active species that are assumed to give reactions involving NO_x. In a more recent study,¹⁷ the kinetics of formation of a hydroxyl radical has been studied in the decomposition of peroxyxynitrous acid, and the first-order rate constants evaluated. In our case, within the reactor, there is always some amount of air present in NO_x, and the reaction in eqs. (10) and (11) can always occur giving hydroxyl radicals within it. These radicals can abstract hydrogen from the resin, which can combine with NO₂ as shown below.

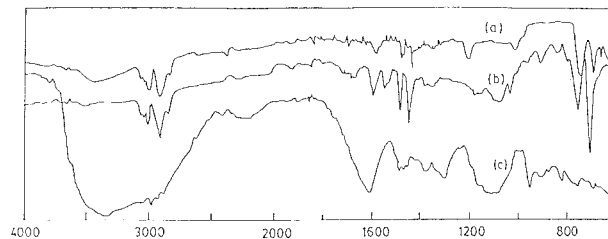
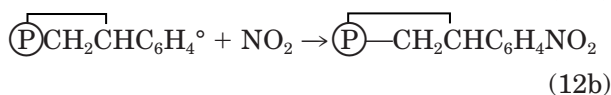
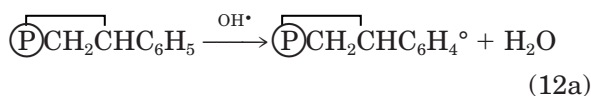


Figure 3 FTIR of (a) unmodified R₁ resin, (b) nitrated R₂ resin, and (c) aminated R₃ resin.

FTIR Analysis of the Resin

FTIR spectroscopy is one of the most useful techniques for identification of functional groups. Functional groups present on the PS-DVB resin after the reaction are determined instrumentally by FTIR (Perkin-Elmer 1600). The PS-DVB resins are 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 R₁ to R₃ resins have been used to determine FTIR spectra shown in Figure 3. There are characteristic sharp peaks of NO₂ present at 700 and 1400, cm⁻¹ for the R₂ resin, which confirms the presence of an NO₂ group on it. In the aminated R₃ resin, there is a strong absorption near 3,100 to 3,200 cm⁻¹, which confirms the presence of a NH₂ group on it with simultaneous disappearance of peaks at 1400 cm⁻¹ belonging to the NO₂ group.

Elemental Analysis through ESCA

For determining the binding energy of different elements presents in the surface of PS-DVB resin, we carried out an ESCA analysis as described earlier. First, we examined the samples of the blank, nitrated, and aminated PS-DVB resins for a survey scan in the range of 0–500 and 500–1000 eV. From this scan, each individual elements (Oxygen O 1s, Nitrogen N 1s, and Carbon C 1s is scanned in its binding energy zone). After doing this, we prepared a scan in the range of 275–325 eV for carbon for those samples. A distinct peak of C 1s for carbon is observed at 284.2 eV in the blank PS-DVB sample, as expected. Thereafter, the nitrated PS-DVB resins 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 carbon binding. Again, in the aminated R₃ resin there is slight shifting in the carbon C 1s peak position, as shown in Figure 4(b). We then scanned Nitrogen N 1s in the range

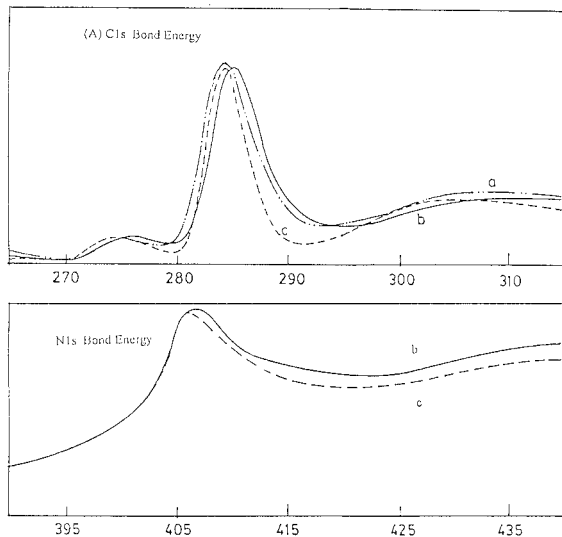


Figure 4 ESCA analysis of (a) unmodified R_1 resin, (b) nitrated R_2 resin, and (c) aminated R_3 resin.

of 400–450 eV for all these three samples. A characteristic peak of nitrogen at 407 eV is present in the nitrogen range of 395–410 eV, as shown in the Figure 4b. The scan of the resins shows the nitrogen N 1s peak at 450 eV, showing a decrease in N 1s binding energy in aminated R_3 resins. This confirms the presence of a bond between carbon and nitrogen and the NO_2 group is attached to the phenyl ring.

Effect of Temperature on Nitration of PS-DVB Resin

It is expected that the extent of nitration reaction would increase with increasing temperature. Therefore, the effect of nitration of R_1 resin is examined by varying the temperature at a step change of 10°C , starting from 60°C up to 140°C . Beyond 140°C , the PS-DVB resins starts becoming brown in color and, therefore, we did not examine temperatures more than this. It is observed that the maximum consumption of NO_x took place at 130 to 140°C . Between 100 to 110°C , the consumption jumps, and thereafter it increases gradually up to 130°C . The resin is then aminated using hydrazine hydrate; thereafter, the exchange capacity of these R_3 resin is determined, and the results are shown in Figure 5 up to 100°C and Figure 6 for temperatures beyond. It is observed that the color of the resin changes from white to pale yellow as we increase the temperature from 60 to 100°C and beyond; this become slightly darker to the naked eye, and the

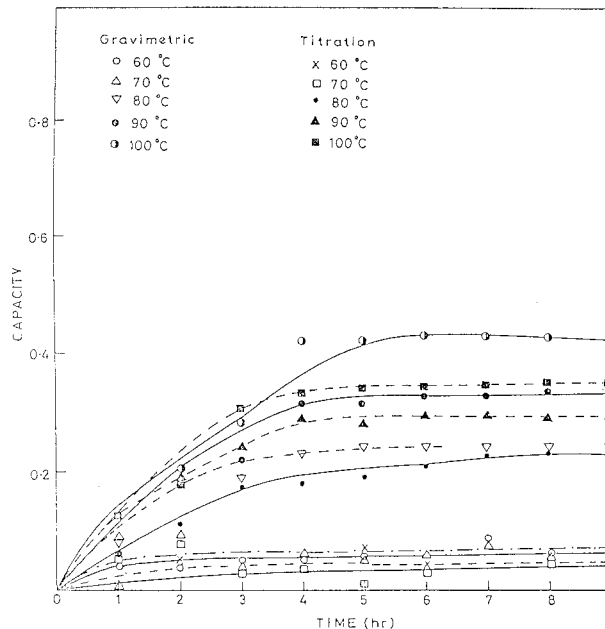


Figure 5 Effect of nitration time and temperature on the one time capacity of R_3 resin for temperatures up to 100°C .

color remains the same as the temperature increases. The capacity results show that the maximum capacity is achieved at $130\text{--}140^\circ\text{C}$.

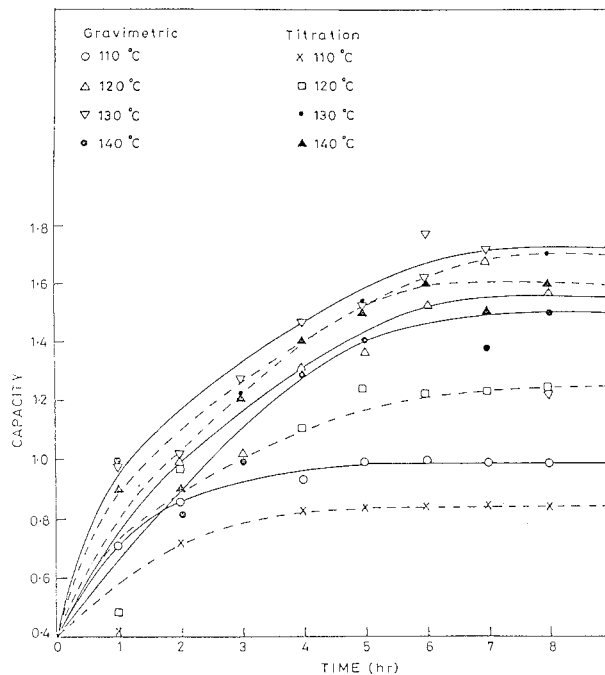


Figure 6 Effect of nitration time and temperature on the one time capacity of R_3 resin for temperatures between $100\text{--}140^\circ\text{C}$.

Because the capacity of the R_3 resin reflects the extent of nitration, it has been experimentally determined by titration and gravimetric estimation techniques, as discussed earlier. We observed that with the increasing reaction time, the extent of nitration first increases rapidly, but reaches an asymptotic value. It is found that the most appropriate temperature to carry out the nitration of R_1 resin is 130°C , and beyond this temperature, there is no significant increase in nitration. Below 100°C almost negligible nitration occurred. The exchange capacity of the aminated R_3 resin in Figures 5 and 6 is a one time value, as these cannot be regenerated from the ASTM procedures, and the need of further modification arises because of this only.

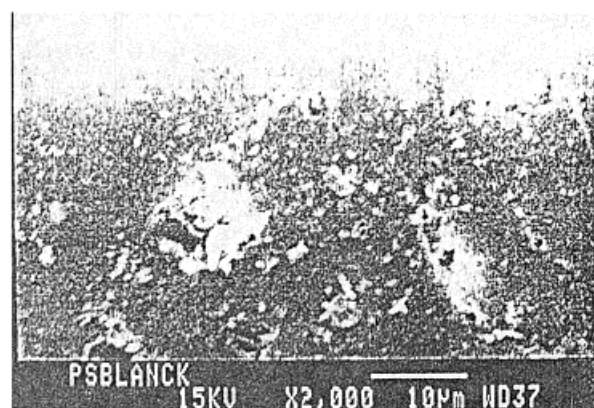
Effect of Modification on Morphology

It is desired to find out changes in the morphology of the surfaces due to modification reactions for which we developed SEM photographs at a $1500\times$ magnification. These are shown in Figure 7 for unmodified resin, after modification by NO_x and then after reducing them to amines groups. From these figures, it appears that these chemical reactions produce a morphological change over the surface. The aminated R_3 resin carries crest over the surface at this magnification, which are few in number but are significant.

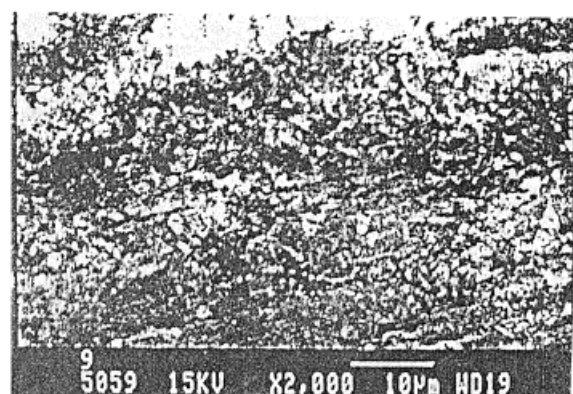
Effect of Modification on Surface Area

As discussed earlier, we determined the internal surface area of polymer particles using standard BET isotherms apparatus (Pulse Chemisorb 2700). We have determined the surface area of unmodified resin, the effect on this on NO_x modification and aminated resins over the time of reactions. The results are shown in Table I, and we see no specific trend in these data. This is because on chemical modification, its ability to retain moisture is considerably increased. We will be showing later that the moisture is held with greater solvation energy, and is difficult to remove. For determination of surface area, the adsorbed moisture of the sample may block pores and may give misleading results. It is desirable that the sample should contain no moisture and should be completely dry for a correct reading. In our case, because of a higher solvation energy of the resin after modification, the information on surface area in Table I could not be trusted.

(a) Unmodified Resin



(b) Surface Nitrated Resin



(c) Surface Aminated Resin

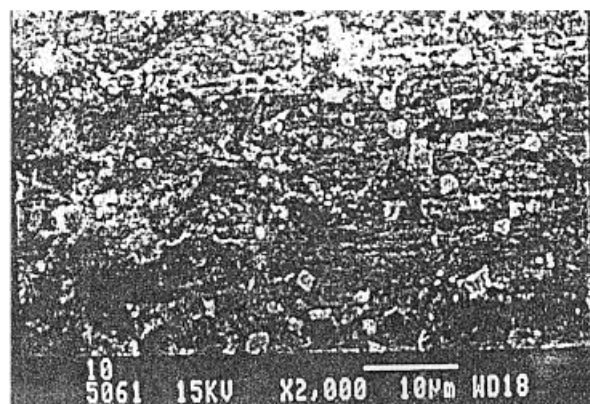


Figure 7 Effect of modification on the surface morphology of PS-DVB resin.

Effect of Chemical Modification of Aminated PS-DVB Resin

Earlier, it was observed that the capacity of aminated R_3 resin goes down to zero during the first regeneration cycle and cannot be further regenerated using the ASTM procedure. This can be explained by the fact that the aniline moiety of the

Table I Change in Surface Area of PS-DVB Resin Due to Modification

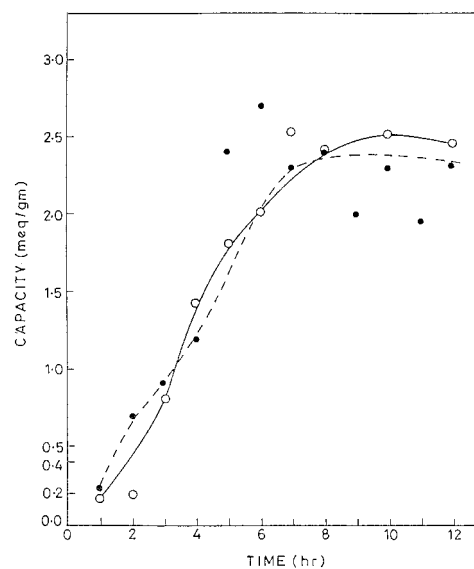
Type of Resin	Surface Area (m ² /g)
Unmodified PS-DVB resin	9.879
Surface nitrated PS-DVB resin	2.447
Aminated PS-DVB resin (1 h)	2.539
Aminated PS-DVB resin (2 h)	2.840
Aminated PS-DVB resin (3 h)	2.861
Aminated PS-DVB resin (4 h)	3.377
Aminated PS-DVB resin (5 h)	3.594
Aminated PS-DVB resin (6 h)	4.135
Aminated PS-DVB resin (7 h)	6.297
Aminated PS-DVB resin (8 h)	5.031
Aminated PS-DVB resin (9 h)	4.938
Dowex from Dow Chemicals	1.243

modified resin has very low pK value, and it was felt that on its further modification, shortcoming of the resin would be removed. As a result of this, these aminated R₃ resins have been further modified, and we now show that these resins can then be regenerated by the procedure given in ASTM standards. In our experimentations, we determined the exchange capacity of a given resin in two consecutive runs, and these capacities were found to be close to each other within the experimental errors.

To make the aminated R₃ resin regenerable, we first modified it with epichlorohydrin to get weak base anion exchange resin. Experimentally, we have shown that the exchange capacity of the resultant resin is doubled, which implies that two molecules of epichlorohydrin are attached to the amine group. The reaction is extremely simple, occurs smoothly, and is associated with slight color change of the resin as shown in Figure 2. In preparing these resins, the parameter that was varied systematically was the duration of nitration, keeping the other factors like time of amination and time of reaction with epichlorohydrin as an invariant. Experiments also confirm that the duration of nitration has considerable effect upon the final capacity of the resin, and the results on the exchange capacity of the R₅ resin have been plotted in Figure 8. This figure shows that for short time of nitration, the capacity of the resin rises, which is expected because the increasing duration of the nitration increases the number of sites of exchanging groups on the resin. However, for longer times, there is a slight fall, which perhaps indicates polymer degradation. From Figure 6 it is seen that aminated R₃ resin gives a maximum capacity of 1.7 mEq/gm, whereas the maxi-

imum capacity of the epichlorohydrin resin (which can be regenerated) is 2.6 mEq/g, which is approximately twice that of R₃ resin. This is because for every amine group generated, two amine groups are created through modification by epichlorohydrin on the resin.

In an alternate modification scheme, the directly aminated resins were refluxed with dichloroethane and then modified by trimethylamine (R₇ resin), triethylamine (R₈ resin), and triphenylphosphine (R₉ resin). To confirm that two dichloroethane molecules are attached, we have refluxed the R₆ resin for 4 h. The chloride group concentration has been determined by precipitation from silver nitrate solution, and was determined to be 2.65 mEq/g, indicating about two molecules of dichloroethane reacting with every amine group. The capacities of these strong base R₇ to R₉ resins have been determined by the similar ASTM procedure and the results are given in Figures 9, 10, and 11. For each experimental data shown in these figures the determination of exchange capacity was similarly performed twice for a given resin in at least two consecutive runs to show that the resins can be regenerated and can be used as an anion exchange resin. The parameter that was systematically varied was once again the duration of nitration, and every sample of the resin was aminated and reacted with dichloroethane identically. The results show that the modified strong base R₇ to R₉ resins have a maximum capacity of around 5 mEq/g of wet resin in all three cases, which occurs after 5 h of nitra-

**Figure 8** Effect of nitration time on the capacity of R₅ resin modified by epichlorohydrin.

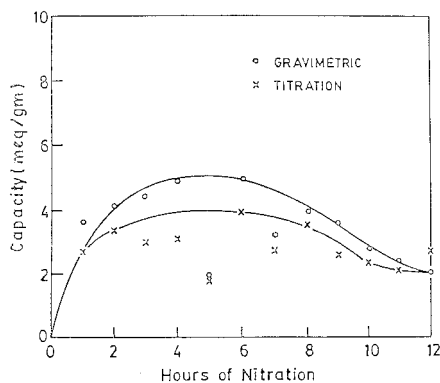


Figure 9 Effect of nitration time on the capacity of R₇ resin quarternized with TMA.

tion, and the slight fall in capacity occurs for a duration of more than this because of the blocking of the pores.

We have determined the capacity over 10 cycles of ion exchange and found that R₇ to R₉ resin can be regenerated by ASTM (and ISI) procedures and, therefore, can be used as anion exchange resin and can replace the commercial resin. We have tested the commercial Dowex resin from Dow Chemicals and it was shown to have a capacity of 1.68 mEq/g of wet resin with 43.15% moisture. This compares with its rated capacity of 3.2 mEq/g of dry resin with a moisture content between 36 to 42%. The jump in the capacity of the R₇ to R₉ anion exchange resins cannot be explained by a simple count of exchanging sites alone. This is because if this was the fact, then the modification with epichlorohydrin would have been equivalent to the modification by dichloroethane, but this was not found to be the case. The figures 9 to 11 show the effect of change in the counter ion from trimethylamine to triethylamine and triphenylphosphine, and are found to have a

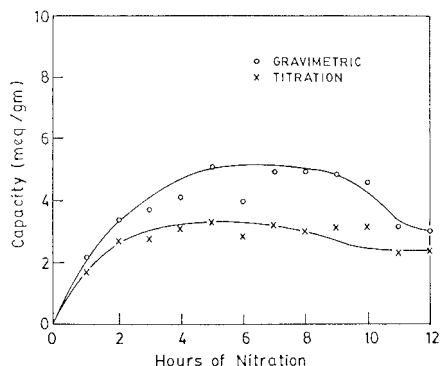


Figure 10 Effect of nitration time on the capacity of R₈ resin quarternized by triethylamine.

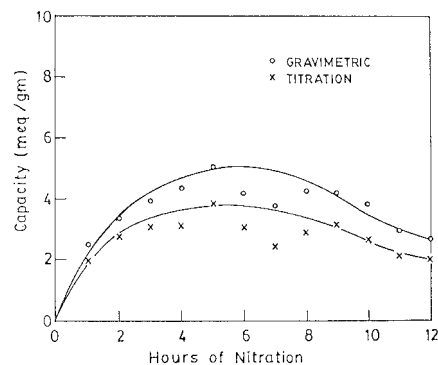


Figure 11 Effect of nitration time on the capacity of R₉ resin modified by triphenylphosphine.

similar trend in all these cases. From these we observe that initially there is a rise in capacity and it undergoes a maximum value followed by a gradual and slow fall, eventually attaining an asymptotic value.

Experiments show that 13.39 millimoles (or 300 mL) of NO_x is consumed for every dry gram of the resin. Figure 9 shows that the maximum exchange capacity of R₅ resin occurs after 6 h of nitration, which is 4.8 mEq/g of wet resin, and we later (see Figs. 12 to 14) show that the resin has a total of 69% moisture on a dry basis. This means that on the dry resin basis, it has a capacity of 4.80/0.31 or 15.48 mEq/g of dry resin, and this just about equals the amount of NO_x fed. It is assumed that there is one NH₂ group on every phenyl ring, the anion exchanging groups would be NH₃⁺Cl⁻ (with a molecular weight of the repeat unit in R₃ $\overline{\text{P}}\text{—CH}_2\text{CHC}_6\text{H}_4\text{NH}_3^+\text{Cl}^-$ as 155.5). If N₀ is the number of repeat units per polymer chain, the theoretical amination would be N₀/(155.5 N₀) or 6.39 mEq/g on a dry basis, a value that is independent of chain length. Because 13.39 mmol of NO_x (which just about shows up completely on the resin) has been reacted, it implies that there is more than one NO₂ appearing in all repeat units (approximately two NO₂ groups per repeat units) of the chain. Secondly, the resin reported in this work has an extremely low surface area with less than a percent of the phenyl rings on the internal pores. This suggests that most of the reaction must be occurring within the polymer gel phase with a negligible reaction on the surface.

Equilibrium Content of Modified Resins

To understand the five times increase on a dry mass basis (compared to commercially available

strong base exchangers) in capacity of PS-DVB resin modified by dichloroethane, one must consider the exchange equilibrium. The resin is represented by a crosslinking network of chains that consists of rigid, rod-shaped segments that carry charges. When the resin is immersed in a water solution of electrolytes, the matrix of the polymer gel stretches like elastic springs to accommodate the water as well as the electrolytes. The study of ion exchange resins for separation has been going on for over 50 years, and there has been a continued effort to synthesize exchangers of higher capacity. These studies¹ have revealed that higher capacities are favored by (a) a low degree of crosslinking, (b) a strong solvation tendency of the fixed ionic groups, (c) a large and strongly solvated counterion, (d) a low valence of counterion, (e) a complete dissociation in the resin, and (f) a swelling due to water of the hydration.

The commercially available anion exchange resin always have "free" moisture and solvent bound in the form of a solvation shell. The water uptake by an initially dry resin is accompanied by swelling of the former. Experiments with commercial resins have shown that the free water can be removed either by centrifugation or by oven drying, whereas the solvation shell moisture can be removed under vacuum at a temperature of 100°C in 24 h. The experiments with our chloroethylated PS-DVB resins reveal that water is quite differently bound, and application of high vacuum and temperature alone are not sufficient to characterize solvation shells.

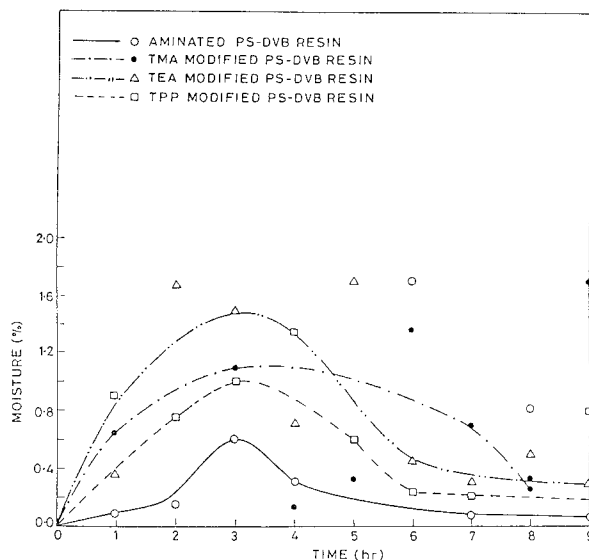


Figure 12 Shell 1 moisture content of modified PS-DVB resin.

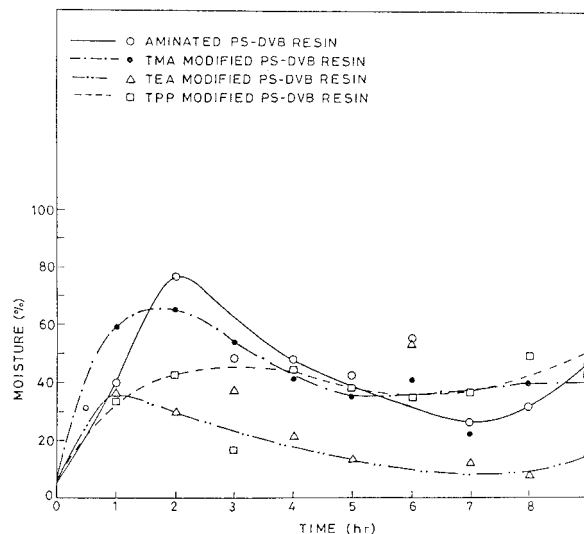


Figure 13 Shell 2 moisture content of modified PS-DVB resin.

We first prepared R_7 to R_9 anion exchange resins for different time durations of nitration in the usual way as described earlier. We then put these in a dessicator (containing P_2O_5) for the 6 months for drying at ambient temperature and vacuum of 750 mm. We determined the mass of these, and called these as dry mass. We subsequently boiled them with distilled water for 4 h and determined their masses after drying them with filter paper. These resins were dried under the three conditions described earlier, and the shell 1 to shell 3 moistures determined. For example, for commercial anion exchange resin (e.g., Dowex from Dow Chemicals) 11.40% moisture was lost in oven drying, thus constituting first-shell moisture, while the 32.13% moisture was lost in the vacuum drying at 100°C in 24 h, this being the second-shell moisture. There was nothing remaining as the third-shell moisture. This gives a total of 43.53% moisture, and compares well with its ratings (i.e., moisture content of 36–42%).

In our case, the unmodified R_1 resin is found to retain a total of 8.59% as first-shell moisture and none as shell 2 and 3 moistures, and this result is expected because the unmodified resins are hydrophobic in nature. However, in the case of strong base R_7 to R_9 resin (results shown in Figs. 12 to 14), the first-shell moisture content first increases as the extent of nitration increases, but it falls for larger times of nitration, and in this way has a maxima and low asymptotic value. This reduction in the shell 1 moisture occurs with a simultaneous fall in shell 2 moisture and an increase in the shell 3 moisture due to an increase

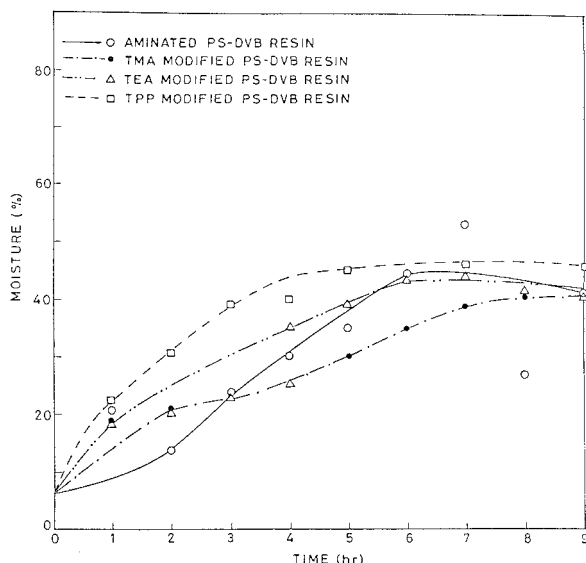


Figure 14 Shell 3 moisture content of modified PS-DVB resin.

in nitration. However, for large times of nitration, moisture in shell 3 is held with a greater energy of interaction and reaches an asymptotic value. We have also examined the effect of the counterions used upon the solvation ability of the resin. A similar trend is observed when the counterions are changed in R_7 to R_9 resin, and these are also shown in these figures. In the case of the triphenylphosphine counter ion, a broad maxima in the shell 1 moisture content is obtained. The initial rise in these curves is similarly explained on the basis of more of a number of anions available in the modified resin. The sharpness in the fall is the highest for aminated resin, while curves for R_9 resin are broad.

Figures 13 and 14 show the effect of the duration of nitration on the second- and the third-shell moistures, and it is seen that the first- and the second-shell moisture falls to give the increased third-shell moisture for larger times of nitration. This clearly indicates that moisture in the R_7 to R_9 resins prepared by us is held with increased interactive forces, this way giving more solvation, and evidently our resins are more hydrophilic. In Figure 14, the asymptotic amount of the third-shell moisture is found to depend upon the counterion used, and is the largest for TPP counterion. For aminated resin where the counterion is NH_4^+ , for a short duration of nitration, the third-shell moisture is the smallest, but for large times of nitration, it surpasses the values for TMA and TEA counterions. It has been already pointed out that solvation energy affects the capacity of the

resin to a great extent, and the increased capacity of the resin developed by us may as well be due to this increased solvation of moisture in the polymer resin.

CONCLUSIONS

The unmodified R_1 resin has been prepared using a suspension polymerization technique using gelatin as the stabilizer. For a gelatin concentration of 0.028 g, the internal surface area of the resin was found to be $8.9 \text{ m}^2/\text{g}$, with an external average particle size of 1 mm. The nitration of these using NO_x is an extremely simple reaction, and the bond formation in the R_2 resin has been confirmed using the Laissagne spot test, FTIR, and ESCA analysis. Evidently on modification, the surface area is expected to change, but the results are not found to be reliable due to absorbed moisture, which does not come out by simple heating. We have developed SEM photographs and examined the effect of chemical modification upon its surface morphology. The surfaces appear to be affected, as seen from SEM analysis.

The weak-base aminated R_3 resin thus prepared cannot be regenerated using the usual ASTM procedure, and to overcome this difficulty, we decided to further modify these resins. The R_5 resin modified by epichlorohydrin is regenerable, gave weak-base anion exchange resin, and has a capacity of approximately twice that of the aminated resin. This suggests that for every amine group produced by nitration, two molecules of epichlorohydrin are reacted.

Considerably more interesting results are obtained when the aminated R_3 resins are modified with dichloroethane to give chloroethylated R_6 resins. The experimental measure of chloride clearly suggests two dichloroethane molecules react with every amine groups. The change from chloromethylation (2.97 mEq/dry g for commercial resin) to chloroethylation increases the exchange capacity of its quarternized R_7 to R_9 resins (15.48 mEq/dry gm) to five times value on dry mass basis. To assess the difference in the solvation ability of chloroethylated resins, we devised three stages of the moisture drying procedure. We showed that unmodified resin had only shell 1 moisture, while commercial chloromethylated strong anion exchange resin has shell 1 (11.40%) and 2 (32.13%) only, and the total of 43.15% moisture compares well with its rated moisture content. As opposed to this, the chloroethylated strong-base resin has largely shell 3 moisture,

and this increased monotonically with the duration of nitration.

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