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Effect of Gas Phase Nitration on Poly(methyl methacrylate) (PMMA) Based Ion Exchange Resins

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Abstract: High-capacity ion exchange resins based on Poly Methyl Methacrylate (PMMA) was developed during this study having higher mechanical strength, stable and, hydrophilic in nature compared to Poly styrene (PS) based systems. PMMA was cross-linked by Di Vinyl Benzene (DVB) to get macro porous PMMA-DVB resins by suspension polymerization. PMMA-DVB resins were surface modified by nitration followed by amination under appropriate temperature conditions. Change in the color of resin from white to pale yellow and pale yellow to golden yellow as well as characteristic peaks of NO_2 at 700 cm^{-1} and 1400 cm^{-1} and 3100-3200 cm^{-1} for NH_2group in FTIR spectroscopy confirmed the presence of NOx and NH_2 groups on the surface of resin. These modified resins were evaluated with respect to the ion exchange capacity and it was found that the modified PMMA-DVB resin possessed higher capacity compared to commercial Poly Styrene- Di Vinyl Benzne resin. This may be attributed to the modification of CH_3/CH_2 sites of PMMA.

Keywords: PMMA, Chemical modification, ion exchanger

1 Introduction

Ionic polymers are polymers containing chemically bonded ions within their structure. Ionic polymers having few ions are melt-process-able thermoplastics (called ionomers), which as those having higher content are either water-soluble polymers (poly electrolyte) or cross-linked polymers (ion exchange resins). Polyelectrolyte and ion exchange polymers are not melt-process-able on conventional plastic processing machinery. Ionic polymers usually contain ionic groups in the range of 10-15-mole % (Cheremisionoff, 1997).

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A number of ionomers based on polyethylene, elastomers, poly tetra fluoro ethylene (PTFE), and poly sulfone have been developed over the years. Poly Ethylene ionomers are transparent, flexible having good impact at low temperature and good resistance to greases /solvents. They are traditionally used in packaging, surface coating on glass bottles to prevent breakage. Ionomers with PTFE backbone and pendant perfluoro sulfonate or perfluoro carboxylate groups are becoming commercially important, though their cost is higher. Originally they were developed to be used as membranes in fuel cell, but now are integral part of separation processes due to their ability to survive under extremely aggressive chemical environment. Ionomers based on poly sulphone are being used as membranes for purifying water in reverse osmosis. They are superior to conventional membranes because of their resistant nature towards oxidation by chlorine, chemicals, and biological fouling along with good compaction under high operating pressure. Ionomers based on ethylene propylene diene tertiary polymer are also in use.

Polyelectrolytes are used in three major applications: Ion exchange resins, Ion exchange membrane, and Heterogeneous catalyst.

A polymer in the form of a thin membrane is typically used as ion exchange membrane. When exposed to electrolyte, a membrane allows only counter ions to pass through it and act as a barrier to complimentary ion (and therefore is said to be perm selective). This principle is exploited in electro dialysis too. High ion content is not necessary for a ion-exchange membrane since its function is governed by its exchange capacity. Ion content of a membrane is between ionomers and ion exchange resins.

Usually ion exchanger are insoluble resins of polymer and their main application is in de ionization or de mineralization of tap water to distilled water. They should posses high ion content. They are inherently water-soluble but to make them insoluble they are chemically cross-linked during the process of synthesis. When immersed in water they swell to a degree, which is inversely related to density of cross-links. The swelling process facilitates rapid ion exchange (Kroschwitz, 1990).

Ionic polymers are hydrophilic in nature having the moderate ion content swell in contact with water and with higher ion content dissolve unless they are cross linked. The hydrophilicity of ionic polymers leads to another type of membrane application that is reverse osmosis and is used for treatment of water in paper mill, pollution control, industrial water treatment, chemical separation and food processing industries.

Polyelectrolyte except cross-linked are soluble in water and number of applications are based on this property. Some of the applications of these resins are as thickeners, dispersants, and flocculating agents. They are used as sizes in textile industry and in paper manufacture. Their application as additive to drilling muds and to soil for conditioning purpose is the demanding area. One of the latest applications in medical field is as dental cement (Chanda and Roy, 1993).

Synthesis of ionic polymers is done by the following methods (Dyson, 1987): Direct Synthesis or by Post funtionalization of standard/ special preformed polymer

In direct synthesis, an aqueous solution of ionic vinyl monomer (acrylic acid) is homo polymerized in aqueous solution. Example of this technique is ethylene with small amount of metha acrylic acid in aqueous emulsion at low pH to suppress the solubility of acid monomer. However, direct synthesis of less ionic polymer which involve co polymerizing ionic with non-ionic is not so simple because two types of monomers are different in their physical and co polymerization characteristics.

Post funtionalization of standard preformed polymers is another technique provided the polymer is reactive, e.g., sulfonation of poly styrene (PS) and grafting on poly butadiene by using free radical. To enhance the reactivity, reactive units are incorporated in the polymer by co polymerization, e.g., sulfonitable ethylene propylene rubber and poly (arylene ether sulfone).

2 Materials and Methods

2.1 Preparation of Macro porous PMMA-DVB Copolymer Resin

In order to get macroporous PMMA- DVB copolymer resins having the size of 1 mm, the method of suspension polymerization was used (Balakrishnan and Ford, 1982; Lewandowski et al, 1992; Egawa et al, 1988). The macroporous resin was prepared by following recipe. Methyl methacrylate (MMA) was used as monomer and DVB as cross-linking agent and recipe consisted of two phases. Organic phase was prepared by mixing MMA (285 g), di vinyl benzene (90 g), azobis iso butyro nitrile (4.5 g) and toluene (200 g). The organic phase was suspended in aqueous phase containing distilled water (1500 ml), sodium sulphate (64 g), calcium carbonate (14 g) and gelatin (0.029g) (Sinha and Kumar, 2002). These phases were mixed and agitated to carryout polymerization at 60 ˚C for 4 hours in a set up shown in the figure 1. After 4 hours, the temperature of the reaction mixture was increased to 90 ˚C in half an hour and kept constant for next two hours. Resins produced had a considerable mechanical strength, were separated and washed with water. To remove the excess calcium carbonate, N/10 HCl solution was added to the resin. The resin was separated, washed with water and finally with methanol and air-dried in oven maintained at 70-75 ˚C. It was observed that the particles start sticking and form a big lump when gelatin content is reduced below 0.028 g. To get the polymer resins of required size, lump needs to be broken which cause significant loss of material and energy. To overcome this difficulty we increased the gelatin content and it was found that 0.029 gm is the most appropriate amount to produce the resins of required size i. e. one mm.

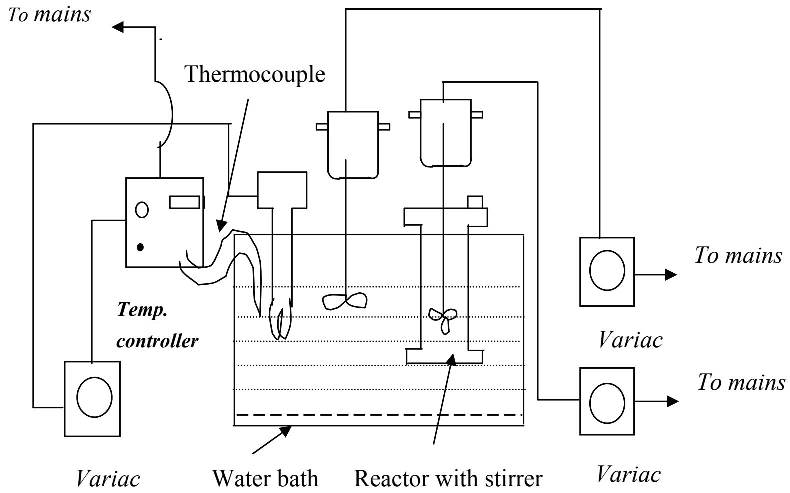


Figure 1: Experimental Setup for Synthesis of PMMA-DVB Resin

2.2 Gas Phase Nitration of PMMA-DVB Resins using NOx

After preparing resins of 1 mm size by the procedure discussed above, resin was subjected to nitration. The literature reports that surface nitration of macro porous PMMA-DVB copolymer usually takes place by reacting it with concentrated nitric acid (HNO_3), which can easily be aminated. However due to use of concentrated HNO_3, particle loose their mechanical strength and get degraded. In addition to this, resins cannot be regenerated for repeated uses and are of no commercial significance.

Direct gas phase nitration of PMMA -DVB resins was carried out in a 2.5-liter reaction vessel as shown in figure 2. This vessel was equipped with an aluminum cap with 1.2 mm opening at the top for injecting gas, which was closed by a silicon rubber septum. A mixture of NO and NO_2 called $NO_x$was generated by reacting sodium nitrite ($NaNO_2$:10 g mole), sulphuric acid (H_2SO_4: sp. gr. 1.18, 25 ml) in the presence of ferrous sulphate ($FeSO_4$, 5 g mole) in 1.5 litre two neck round bottom flask (Sinha et al., 2001) . The container was equipped with rubber septum for withdrawing NOx with the help of a 100 ml syringe. The generation of NOx

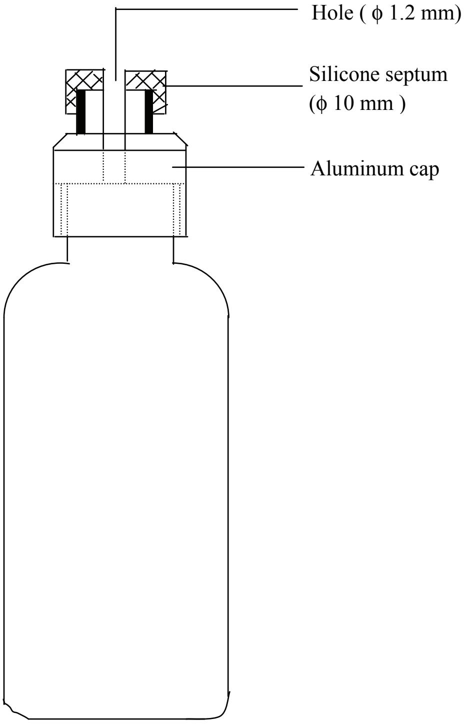


Figure 2: Reactor Used for Nitration of PMMA-DVB Resin

took place as per the reactions given below.

$2\ NaNO_2 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_2$ (1a)

$3\ HNO_2 \rightarrow H_2O + HNO_3 + 2\ NO$ (1b)

$FeSO_4 + NO \rightarrow [Fe, NO]\ SO_4$ (1c)

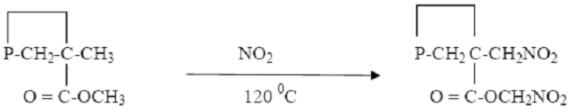
$2\ NO + O_2 \rightarrow 2\ NO_2$ (1d)

Approximately 1.5 g of PMMA-DVB resins were introduced in the reaction vessel and vessel was placed in an oven maintained at 120 °C temperature. A small needle was punctured through silicon septum of the reaction vessel as to allow a thermal equilibrium with oven. The gas inside the bottle expanded due to heating and escape through needle. The needle was removed and the vessel was taken out to cool at room temperature. This created slight vacuum inside the vessel so that NOx could be introduced in the bottle and total pressure remained approximately one atmospheric (atm.). After feeding required amount of gas mixture, the vessel was again kept in oven maintained at desired temperature. Reaction was carried out for 10 hrs in ten different bottles. Bottles were withdrawn on hourly basis and allowed to cool at room temperature. Color of nitrated resins changed from white to pale yellow as shown in figure 3. The amount of consumed NO_x was determined by dissolving it into 100 ml of distilled water and subsequent titration with NaOH

There were few problems associated with evaluation of consumed NOx. It was very difficult to dissolve all the NOx completely and we found that on opening the cap of reactor for pouring the distilled water, some amount of the unreacted NOx always discharged to atmosphere. This is likely to affect the results; however we endeavored to minimize this loss. Finally polymer resins were washed, dried and kept in a dessicator.

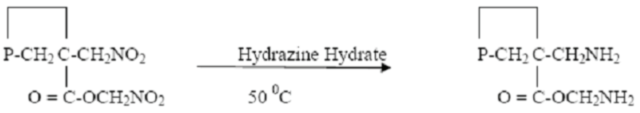
2.3 Amination of Surface Nitrated PMMA-DVB Beads

To reduce NO_2 functional group into amine groups on the surface of PMMA-DVB resins, the resins were refluxed with hydrazine hydrate. 1.5 gm of surface nitrated PMMA-DVB resins were placed in a conical flask with 50 ml of hydrazine hydrate. The reaction mass was refluxed at 50 ˚C for 4 hours in an oil bath maintained at 60 ˚C. After reflux was over, the resins were subjected to filtration, washing with distilled water and dried. Color of resin changes from pale yellow to golden yellow as shown in figure 3. These aminated resins were subjected to further processing and determination of capacity.



$$P\text{-}CH_2\text{-}\underset{O=C\text{-}OCH_3}{\underset{|}{C}}\text{-}CH_3 \xrightarrow[120\ ^{0}C]{NO_2} P\text{-}CH_2\,\underset{O=C\text{-}OCH_2NO_2}{\underset{|}{C}}\text{-}CH_2NO_2$$

Nitration of PMMA-EDMA Beads



$$P\text{-}CH_2\,\underset{O=C\text{-}OCH_2NO_2}{\underset{|}{C}}\text{-}CH_2NO_2 \xrightarrow[50\ ^{0}C]{\text{Hydrazine Hydrate}} P\text{-}CH_2\,\underset{O=C\text{-}OCH_2NH_2}{\underset{|}{C}}\text{-}CH_2NH_2$$

Amination of PMMA-EDMA Beads

(2)

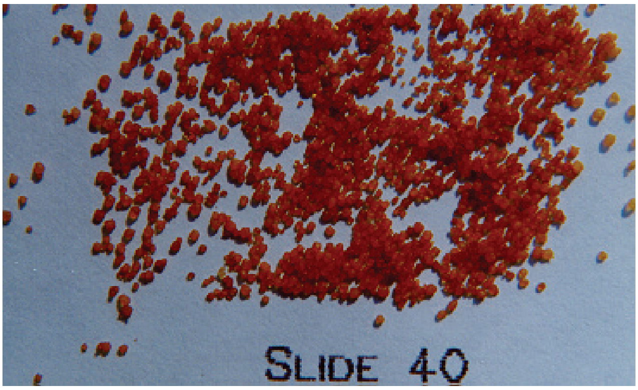
2.4 Characterization of PMMA-DVB Resin: Elementary Test for Nitrogen Detection in PMMA -DVB Resin

In order to detect the nitrogen over the surface of PMMA -DVB beads, modified Lassaigne element spot detection test was used. Here polymer resins were fused with metallic sodium to form sodium cyanide.

$$Na + C + N \rightarrow NaCN \tag{3}$$

Unmodified PMMA-DVB resin

Nitrated PMMA-DVB resin



Aminated PMMA-DVB resin

Figure 3: Effect of modification on PMMA-DVB resins

The entire content was washed with water and 2-3 ml of this filtrate solution was poured into a test tube containing 0.1 –0.2 gm of powdered iron sulphate crystals to give sodium ferrocynide and sodium sulphate after heating.

$$FeSO_4 + 6\,NaCN \rightarrow Na_4[Fe\{CN\}_6] + Na_2SO_4 \quad (4)$$

Addition of 2-3 drops of ferric chloride solution and finally acidified with conc. hydrochloric acid prussian blue color of ferric ferrocynide confirmed the presence of nitrogen in the sample (Li et al., 1995)

$$3\,Na_4[Fe\{CN\}_6] + 4\,FeCl_3 \rightarrow Fe_4[Fe\{CN\}_6]_3 + 12\,NaCl \quad (5)$$

2.5 Determination of NOx Consumed During the Reaction

The unreacted NOx was determined by dissolving it in distilled water. 100 ml of distilled water was added to reactor to dissolve the unreacted NOx by vigorous mixing. This process converted the residual gas into nitric acid (HNO_3) as per the reactions shown.

$$2\,NO_2 + H_2O \rightarrow HNO_3 + HNO_2 \quad (6a)$$

$$3\,HNO_2 \rightarrow HNO_3 + 2\,NO + H_2O \quad (6b)$$

$$4\,NO + 3\,O_2 + 2\,H_2O \rightarrow 4\,HNO_3 \quad (6c)$$

Polymer resin was separated and filtrate consisted of HNO_3 solution, which was pale yellow in color. This solution was titrated with N/10 NaOH to find out the strength of HNO_3 in water and consumed NOx was calculated from the amount of NOx introduced initially. Consumption NOx after every interval of time is given in table 1. It is observed that with increase in time, the NOx consumption first increases and attains maxima at 7h and then tends to decrease as shown in Fig. 4.

2.6 Determination of Capacity by Gravimetric Method

Alternatively the exchange capacity of aminated resin was determined using the method given in ASTM (No. 2187, 2687, 3087, 3375) and BIS (No.110). First of all, mixed acid was 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 was made up to 1000 ml adding distilled water. After this test, water was prepared by diluting mixed acid with distilled water up to 1 % concentration. This water was added to the aminated resin in a quantity of 100 ml per gram and kept for 24 hrs. Resins were filtered and washed with distilled water till filtrate become neutral, which was observed by whether color of methyl orange changes from orange to

Table 1: Volume of NO_x Consumed (in ml/1.5 gm) During Nitration of PMMA-DVB Resin at 120 ˚C

Duration of nitration (hrs)	Nitrated volume of NaOH (ml)	Normality of HNO_3	Unconsumed NOx during nitration (ml)	Consumed NOx during nitration (ml)
1	92.0	0.184	412.16	37.84
2	66.5	0.133	297.92	152.08
3	66.0	0.132	295.68	154.32
4	60.5	0.121	271.04	178.96
5	51.1	0.102	228.48	221.52
6	46.0	0.092	206.08	243.92
7	39.2	0.078	174.72	275.28
8	40.5	0.081	181.44	268.56
9	44.5	0.089	199.36	250.64
10	45.8	0.092	206.08	243.92

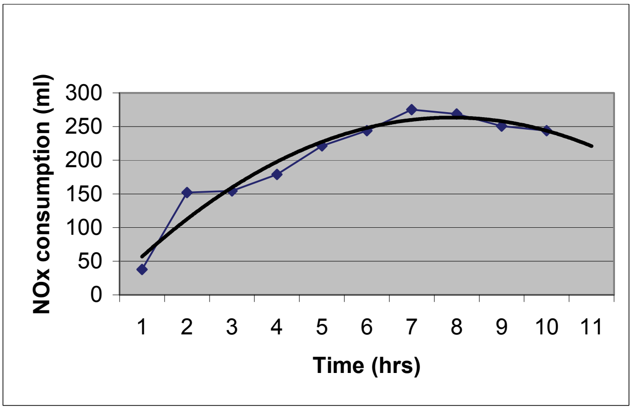


Figure 4: Effect of time on the consumption of NO_x

red or not. Thus we got the resin, which was free from the mixed acid. This resin was mixed with 0.1 N $NaNO_3$ solution (8.5 gm in 100 ml distilled water) and kept for another 24 hrs. Reaction mass was filtered and filtrate was added to 1.7 gm of $AgNO_3$ with 2-3 drop of HNO_3 and entire mass was kept for 24 hrs. The chlorine ion present in the filtrate forms AgCl that was precipitated. This precipitate was filtered, weighed and ion-exchange capacity of aminated resins was calculated by using the following equation.

Capacity (meq/gm) =

$$[\text{Weight of the precipitate x } 1000 / \text{Molecular Weight of AgCl}] \div \text{gm of resin} \quad (7)$$

Calculated capacity of ion-exchange resin is given in table 2. It is found that capacity first increase and reaches to maximum after seven hours before decreasing finally as shown in the figure 5.

2.7 Characterization of PMMA-DVB Resin by Instrumental Methods

FTIR spectroscopy is one of the most useful techniques for the identification of functional groups in the polymers (Willard et al., 1986). Functional group present on the surface of PMMA-DVB polymer were determined instrumentally by this technique (Perkin Elmer 1600). Polymer resins were first grounded into fine powder and mixed with potassium bromide. Pellets of one cm size were prepared by hydraulic press and samples of blank, nitrated and aminated resins were used to determine the FTIR spectra. There was a characteristic sharp peak of NO_2 at 700 cm^{-1} and 1400 cm^{-1} in surface nitrated PMMA-DVB beads. This confirmed the

Table 2: Capacity of Aminated Resin by Gravemetric Method

Duration of nitration (hrs)	Amount of polymer resins(gm)	Weight of ppt. for two consecutive runs (gm)	Capacity in (milli eq. per/gm)	Average capacity (milli eq. / gm)
1	0.6000	0.1576 0.1421	1.83 1.65	1.74
2	1.01706	0.4333 0.4264	2.97 2.92	2.95
3	0.7500	0.3709 0.3622	3.45 3.37	3.41
4	0.7572	0.4046 0.4191	3.72 3.86	3.79
5	0.7001	0.3918 0.4242	3.90 4.22	4.06
6	0.7057	0.4917 0.4829	4.85 4.77	4.81
7	0.7374	0.5176 0.5081	4.89 4.80	4.84
8	0.7500	0.4876 0.4722	4.53 4.39	4.46
9	0.7000	0.3972 0.3647	3.95 3.63	3.79
10	0.7517	0.3560 0.3674	3.30 3.40	3.35

presence of NO_2 group on the surface of PMMA-DVB resin. In the surface aminated sample of PMMA-DVB resin, there was a strong absorption at 3100-3200 cm^{-1} confirming presence of NH_2 group on the surface of PMMA-DVB resins with simultaneous disappearance of peak at 1400 cm^{-1}, which belongs to NO_2 group.

3 Result and discussion

3.1 Suspension Polymerization of PMMA-DVB Resin

Cross-linked macro porous PMMA- DVB copolymer was produced in the form of resins as per the recipe given above. Suspension polymerization is the best method to get polymer in the form of beads. Gelatin content plays a very important role in controlling particle size distribution. It was found that with increase in gelatin

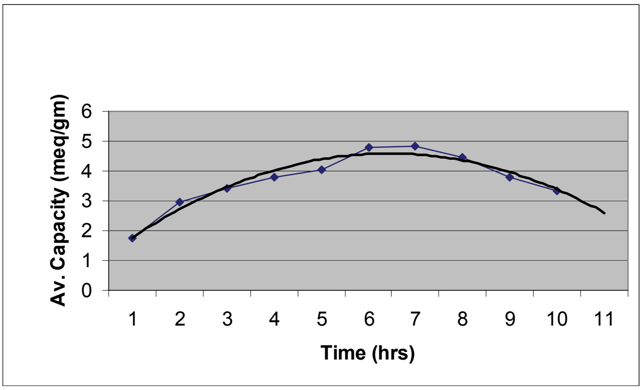


Figure 5: Effect of time on the average capacity of PMMA-DVB resin

content, size of resins gets reduced and there is a critical concentration of gelatin below which resins are unstable and form agglomerates. We used initially 0.028 gm of gelatin and it was found that this amount of gelatin caused formation of big lumps and entire reaction mass become sticky in nature. In order to get the required resin size, this lump needs to be broken causing wastage of energy and material. To overcome this problem, the amount of gelatin content was increased to 0.029 gram, which is the optimum value to get particle size of resinsapproximately 1 mm in diameter. Resin thus obtained was macro porous in nature because use of toluene as diluent which was present in the organic phase.

3.2 Nitration of PMMA-DVB Beads

Produced resins were sieved to have uniform size i.e. 1 mm and were subjected to nitration as per the procedure mentioned above. It was found that copolymer tends to degrade at 130 ˚C (Konar et al., 1998). Therefore we carried out the experimentation at 120°C for ten hours. The effect of time on nitration was examined by withdrawing bottles after an interval of one hour. Color of nitrated resin changed from white to pale yellow. The change in color indicates extent of nitration over the surface of PMMA-DVB resin. Amount of NOx consumed during nitration after each hour was determined as per the procedure mentioned above and experimental results are given in table 1. NOx consumption with time is shown in figure 4. It was observed that with increase in reaction time, the NO_x consumption decreased and was maximum after seven hours and finally decreased. This decrease is possibly due to blockage of pores in PMMA-DVB resin with extent of nitration and high reaction temperature. Moreover, the degree of crosslinking plays a vital role. It was difficult to dissolve NOx completely since at the time of pouring of distilled water, some of NOx gets discharged to atmosphere. This affects the result, so attempt was made to keep these losses to minimum.

3.3 Amination of PMMA-DVB Beads

Nitrated resin was aminated as per the procedure mentioned above and capacity was calculated by the gravimetric method discussed earlier. Extent of amination was made visible by change in color, i.e. golden yellow from pale yellow. Extent of surface modification was evaluated in term of the ion exchange capacity and plotted with time in figure 5. It is found that the capacity of resins increases with time and approaches to maximam after seven hours before decreasing finally. This is in agreement with the consumption of $NO_{x.}$

3.4 Characterization of PMMA-DVB Beads

In order to check the presence of NOx and NH_2 groups on the surface of PMMA-DVB resin, chemical and instrumental analysis were carried out. In case of nitration, color of resin changed from white to pale yellow and in amination from pale yellow to golden yellow. In order to confirm attachment of nitrogen on the surface, a modified Lassaigne test was carried out. Prussian blue color at the end of test confirmed presence of nitrogen over the sample. FTIR spectroscopy was carried out to confirm presence of these groups on polymer surface. Characteristic peaks of NO_2 at 700 cm^{-1} and 1400 cm^{-1} were present in surface nitrated PMMA-DVB resins compared with 3100-3200 cm^{-1} for NH_2 group.

3.5 Exchange Capacity of resin

In order to assess the effect of nitration on the capacity of PMMA-DVB resin the capacity of resin was determined on hourly basis. It was found that the first capacity of modified resin increased and attained a broad maxima and then decreased. The broad maxima attained at 7h of nitration and was in agreement with the results obtained after the nitration. The maximum capacity of this modified resin was observed as 4.84 meq/gm, which is higher than the Polystyrene- Divinyl benzene resin. It also indicative of the modification at various CH_3/CH_2 sites of PMMA resin and is comparable with the results reported in the literature.

3.6 Reproducibility of capacity

We have examined the reproducibility of experimental results in terms of capacity for two consecutive runs and not much deviation was observed as shown in table 2.

4 Conclusion

In this study PMMA-based ion exchange resins were developed by the method of suspension polymerization followed by surface modification. Resins obtained from suspension polymerization have technological applications as ion exchange resins, catalyst carrier, various molding articles etc. In surface modification, latest techniques such as nitration and amination have been used, which are very simple and effective. The observed higher ion exchange capacity of resins indicates the more exchangeable sites available in the polymer.

The resin obtained was observed to have a good mechanical strength, to be more hydrophilic than PS-DVB copolymer, macro porous in nature, and with a higher exchange capacity.

The PMMA ion exchange resins based on weak base have a capacity of ion exchange of 4.84 meq/gm which is much higher than modified PS resin showing considerable improvement. The higher ion exchange capacity of these resins is obvious due to increased surface modification as well as the presence of higher number of sites available for modification; such a feature can be advantageous in a number of commercial applications such as ion exchange resins, ion exchange membrane, and additives.

There is a huge potential for developing these materials by other chemical techniques such as sulphonation, chloro methylation etc. These materials can be used in water purification, as soil conditioner in agricultural applications and as additives in textile and paper industries in future.

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