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STUDIES ON PREPARATION AND PROPERTIES OF MELAMINE, M – NITRO ANILINE AND FORMALDEHYDE (MMNAF) ANION EXCHANGE RESIN

Netal N Chudasama

Department of Chemistry, Gujarat University, M. G. Science Institute, Ahmedabad-38009, Gujarat, India
E-mail : pandenetal2016@gmail.com

Abstract Generally, ion exchangers are ion exchange resins (functionalized porous, organic gel polymer), zeolites, montmorillonite, clay, and soil humus. Ion exchangers are either cation exchangers that exchange positively charged ions (cations) or anion exchangers that exchange negatively charged ions (anions). There are also amphoteric exchangers that are able to exchange both cations and anions simultaneously. However, the simultaneous exchange of cations and anions can be more efficiently performed in mixed beds that contain a mixture of anion and cation exchange resins or passing the treated solution through several different ion exchange materials.

For the synthesis of ion-exchange resins Melamine, m – Nitro Aniline and Formaldehyde (MMNAF), m – nitro aniline was reacted with formaldehyde and melamine using hydrochloric acid as a catalyst. These resins were characterized by elemental analysis. Synthesized resin shows ion exchange capability. Ion exchange resin also showed reusability and stability at an elevated temperature. The synthetic resin is used primarily for purifying water but also for various other applications including separating out some elements. Ion exchange materials are insoluble substances containing loosely held ions which can exchange with other ions in solutions which come in contact with them. These exchanges take place without any physical alteration to the ion exchange material. Ion exchangers are insoluble acids or bases which have salts which are also insoluble, and this enables them to exchange either positively charged ions (cation exchangers) or negatively charged ions (anion exchangers).

Keywords : Ion-Exchange, Melamine, m–Nitro Aniline, Formaldehyde, Thermal Stability, pH titration curve

Introduction

Ion exchange is a reversible interchange of one species of ion present in an insoluble solid with another of like charge present in a solution surrounding the solid. Ion exchanger is used in the process of purification, separation, and decontamination of aqueous and other ion-containing solutions with solid polymeric or mineral ion exchangers.

Ion – exchange can be defined as a reversible exchange of ions between a solid phase and a liquid phase in which there is no appreciable change in the structure of the solid. In this definition, the solid phase is the exchanger materials either inorganic or organic. Materials with fixed positive groups and exchanging anions are called anion exchanger and materials with fixed negative groups and exchanging cations are called cation exchanger. There are others which exchange either cation and anion depending on the pH of the solution, these are termed as amphoteric exchangers. Ion exchange is also possible between two phases. The conventional cation or anion exchangers are available in solid or liquid form.

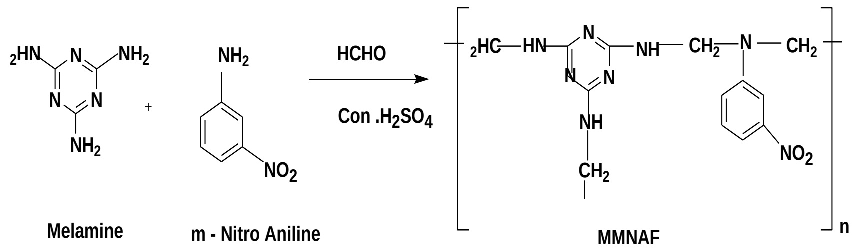
Today, ion – exchange resin is firmly established as an unit operation. Numerous plants are in operation all over the world using these materials for applications ranging from the recovery of metals from industrial wastes to the separation of rare earths .in the laboratory, ion exchangers are used in analytical and preparative chemistry.

Ion exchanges can be unselective or have binding preferences for certain ions or classes of ions, depending on their chemical structure. This can be dependent on the size of the ions, their charge, or their structure.

Preparation of Melamine - m–Nitro Aniline – Formaldehyde (MMNAF) ion – exchanger

Anion – exchange resins were synthesized by the reaction of m–Nitro Aniline with melamine and formaldehyde.

12.6 grams of melamine(0.1 mole) and 30 grams of formaldehyde(1 mole 90 ml of 37% formaline) were taken in 500 ml capacity round bottom three neck flasks, fitted with a stirrer, a thermometer and condenser. The content of the flask was warmed on water bath for about 70˚ C with stirring till all the melamine dissolved. To this was added 3.45 gm of m – Nitro Aniline(0.025 mole) and 13 ml of concentrated sulphuric acid as catalyst and the reaction mixture was heated at 90˚C - 95˚C under reflux conditions for about 1.45 minutes with continuous stirring. The reaction mixture gelled into a dark red soft butter like mass. Now the stirring and heating was stopped, and the gel was removed from the reaction vessel and cured in an electrically operated oven at 90˚C for twenty hours. The red transparent hard mass was crushed to proper mesh size and the sieved resin was stored for further experimental work[i].



Properties of MMNAF ion-exchanger

1) Determination of moisture contents: About 1 gram of the air-dried resin in the free base form was accurate weighed in a weighing bottle and heated at 100˚ C for 24 hours in an electrically operated oven. The loss in weight was recorded and from a constant value obtained, the percentage moisture content was calculated.

2) Determination of exchange capacity: About 0.5gram of the air-dried ion-exchange resin in the free base form was weighed in 100ml conical flask and equilibrated with 50ml of 0.1N HCl in 1N NaCl solution. The acid consumed (Neutralized) after 24 hours was determined by titrating aliquot of the solution with standard alkali.

3) pH titration curve: 0.05 gram of the MMNAF resin in the free base form were weighed accurately and transferred to 100ml glass stoppered flasks. Different volumes of 1N NaCl solution and 0.1N HCl in 1.0N NaCl solution were added, keeping the total volume 50ml. The flasks were equilibrated for 24 hours with occasional shaking. A preliminary experiment showed that 24 hours was sufficient to obtain constant pH. Blank solution was also kept without the resin. Aliquot were withdrawn and titrated for alkalinity or acidity, as the case may be. From the difference in titre values of blank and the supertant solution, the capacities of the resins at different pH values were calculated[iii].

4) Porosity: Take 1–2-gram sample in a small weighing bottle, were first dried in an oven for one day. Sample then reweighed. The lid of the bottle was opened and the weighed bottles with the sample and the lids were then transferred to desiccators containing CCl_4. The contents were allowed to equilibrate in CCl_4 for certain hours. The bottle with samples was then reweighed. The pore volume was calculated from the gain in weight of the samples recorded[v].

5) Thermal stability 1 gram of the resin was placed in a glass ampoule with 20 ml of distilled water. The ampoule was sealed and placed in a constant temperature oven adjusted to the required temperature (80 ̇C,100 ̇C and 120 ̇C). After 24 hours the ampoule was removed and the supertant solution was filtered and the resin was washed with distill water repeatedly. The filtrate and the washing were diluted to a known volume. Acidity or alkalinity if any was determined by titrating an aliquot with standard alkali and acid respectively[ii].

6) Rate of exchange ($OH^{-} \rightarrow Cl^{-}$ Exchange) The free base form of the resins was equilibrated separately with 50ml of 0.1N HCl solution for different time intervals with intermittent shaking. At the end of definite predetermined intervals, the solutions were decanted, and a known volume was titrated against standard alkali to determine the quantity of acid consumed. From this the percentage of capacity realized at different time intervals was calculated.

Result and discussion

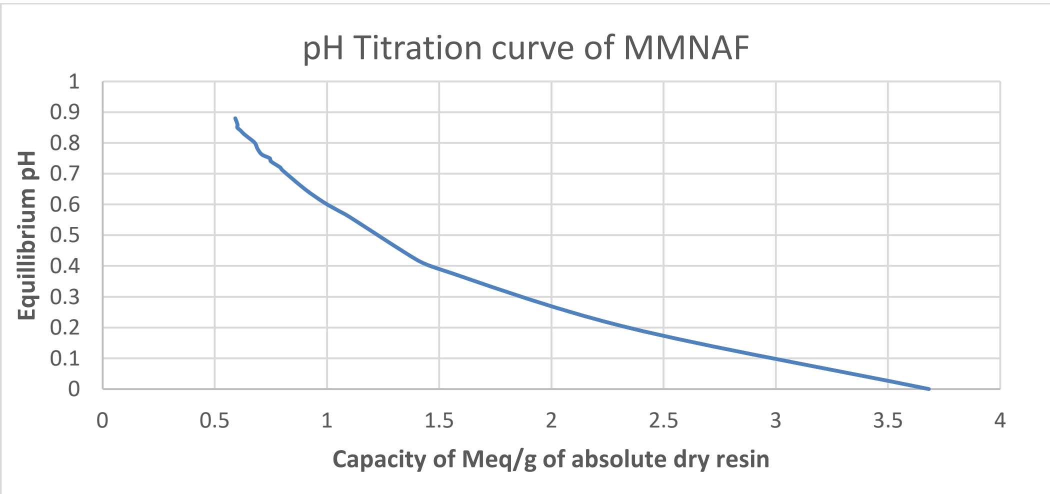
1) Properties of ion exchange resins

No.	Moisture content %	Wet absolute density gm /ml	Total capacity meq/gm of absolute dry resin
1	15.5	3.831	0.887

2) pH titration study of MPTF in the free base form in the presence of 1.0N NaCl

No.	Volume of NaCl ml	Volume of HCl in NaCl ml	Equilibrium pH	Capacity meq/gm of absolute dry resin
1	00.0	50.0	0.591	0.880
2	02.5	47.5	0.601	0.860
3	05.0	45.0	0.600	0.850
4	07.5	42.5	0.615	0.840
5	10.0	40.0	0.628	0.830
6	12.5	37.5	0.645	0.820
7	15.0	35.0	0.678	0.800
8	17.5	32.5	0.691	0.780
9	20.0	30.0	0.710	0.762
10	22.5	27.5	0.745	0.750
11	25.0	25.0	0.750	0.740
12	27.5	22.5	0.792	0.720
13	30.0	20.0	0.800	0.712
14	32.5	17.5	0.901	0.650
15	35.0	15.0	0.985	0.607
16	37.5	12.5	1.050	0.580
17	40.0	10.0	1.099	0.560
18	42.5	07.5	1.400	0.420
19	45.0	05.0	1.500	0.390
20	47.5	02.5	2.340	0.200
21	50.0	00.0	3.682	0.000

Graphical representation of pH titration curve



3) Thermal stability of resin

Temperature	Capacity meq/gm of absolute dry resin	% loss in capacity of resin as determined after heating (in the free base form)	% loss in capacity of resin as determined after regeneration (in the free base form)
80˙˙C	0.887	0.90	0.887
100˙C	0.887	0.90	0.750
120˙C	0.887	0.90	0.600

Scope of the present work

Literature evidence has clearly shown that various raw materials can be used for the synthesis of different ion – exchange resins. In order to be self-dependent on the choice of raw materials, systematic investigations have been carried out in the laboratory to screen various raw materials. In the present investigation the raw materials selected are these which are readily available within the country. The series of anion exchangers has been synthesized which are not commercially available in the country. The aim has to show efficiency of these materials for the purpose for which they were synthesized. Melamine has been used as a cross-linking agent to obtain anion- exchange resins.

Conclusion

During the investigation reported here only indigenously available raw material was used. Properties of the resins such as capacity, wet absolute density, porosity and pH titration curves were studied by the conventional methods as adopted for various ion- exchange reins. The result showed that the anion – exchanger resins were functioning as weak base anion exchangers. From the porosity value, it is revealed that MMNAF has higher porosity value. Data in the table revealed that the synthesized anion exchangers could be used safely up to 80˙C. Above 80˙C, these resins were susceptible to temperature, resulting in lowering in capacity.

Thermal stability of MMNAF in the hydroxyl and chloride form is higher than another anion exchanger.

It is well established fact that the anion exchangers are more stable in their salt form as compared to their hydroxyl form.

An attempt was made to elucidate the structure of the resins by determining their elemental analysis. These values were compared with the elemental content experimentally determined and were found to be almost similar.

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