Preparation and Comparative Studies on Physical Properties of MUF, MAF and MOTF Ion-Exchange Resin

NETAL N. CHUDASAMA
Department of Chemistry,
M. G. Science Institute, Ahmedabad, Gujarat, India

Abstract:

An ion exchange resin is a resin or polymer that act as a medium for ion exchange. It is an insoluble matrix (or support) normally in the form of small microbeads. The beads are typically porous, providing a large surface area on and inside them. The trapping of ion occurs along with the accompanying release of other ions and thus the process is called ion exchange resin.

Ion exchange materials also contain the far less stale bonds between functional groups and the polymer matrix. For this reason, the thermal stability of ion exchange material is mainly based on behaviour of the functional groups, which are responsible for the ion-exchange. In this study the swelling /shrinking properties of different ion –exchange materials have been studied in air and water as a function of the drying time and temperature. The air-dried resins were used as the reference material. Prepared ion exchange resin is stable upto 120°C.

Keyword: *Melamine, Formaldehyde, Urea, Aniline, O-Toluidine*

---

1. Introduction

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 or anion depending on the p^H 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. The most important use of the membranes is in the demineralisations of water besides other application. Ion-exchange resins are used for the removal of calcium, magnesium, iron, and manganese salts from water (water softening), purification of sugar, in hydrometallurgy and for concentration of valuable elements, such as gold, silver, and uranium from mineral ores.

2. Classification of ion – exchange materials

1. Mineral ion exchangers
2. Synthetic inorganic ion exchangers
3. Ion – exchange coals or carbonaceous exchangers
4. Organic ion exchangers of natural and modified type
5. Synthetic organic ion exchangers
    i. Anion exchangers
    ii.Cation exchangers

3. Other ion – exchange materials

1.Amphoteric ion – exchange resins
2.Liquid ion exchangers
3.Macroreticular ion – exchange resins
4.Specific ion exchangers
5.Electron exchangers
6.Redox ion exchangers

Application of ion – exchange resins are extremely varied with regards to types of solutions treated and principles governing such treatment. However, water treatment (softening), demineralization and deionization are still the major applications for these versatile tools.

Literature study 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. Also need for an indigenously available crosslinking agent has been felt and for this purpose many different monomers have been tried. In the present investigation the raw materials selected are these which are readily available within the country. A series of anion exchanger has been synthesized which are not commercially available in the country. The aim has been to show efficiency of these materials for the purpose for which they were synthesized.

Melamine has been used as a crosslinking agent to obtain anion- exchange resins. In this investigation following anion- exchange resins were synthesized from:
1.Melamine – urea – formaldehyde (MUF)
2.Melamine – aniline – formaldehyde (MAF)
3.Melamine – o- toluidine – formaldehyde (MOTF)

4. Experimental Section

Synthesis of anion - exchange resins
Melamine was used as crosslinking agent for the synthesis of the resins.
Anion–exchange resins were synthesised by the reaction of urea, aniline, o-toluidine with melamine and formaldehyde.
The following resins were investigated.

1. **Melamine –Urea – Formaldehyde (MUF) ion – exchange resin**: 6 grams of melamine and 15 grams of formaldehyde were taken in 500 ml capacity round bottom three neck flask, fitted with a stirrer, a thermometer and condenser. The content of the flask were warmed on water bath o about 70˙ C with stirring till all the melamine dissolved. To this was added 3grams of urea and the reaction mixture was heated at 90˙C under reflux conditions for about 3 hours with continuous stirring. The reaction mixture gelled into a hard 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. The transparent hard mass was crushed to proper mesh size and the sieved resin was stored for further experimental work.
2. **Melamine - Aniline – Formaldehyde (MAF) ion – exchange resin:** 6 grams of melamine and 15 grams of formaldehyde were taken in 500 ml capacity round bottom three neck flask, fitted with a stirrer, a thermometer and condenser. The content of the flask was warmed on water bath o about 70˙C with stirring till all the melamine dissolved. To this was added 4.7grams of aniline and the reaction mixture was heated at 95˙C under reflux conditions for about 35 minutes with continuous stirring. The reaction mixture gelled into a hard mass in about 15 minutes. 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 24 hours. The reddish transparent hard mass was crushed to proper mesh size and the sieved resin was stored for further experimental work.

3. **Melamine-o-Toluidine-Formaldehyde (MOTF) ion exchange resin**: 6 grams of melamine and 15 grams of formaldehyde were taken in 500 ml capacity round bottom three neck flask, fitted with a stirrer, a thermometer and condenser. The content of the flask was warmed on water bath o about 70˙ C with stirring till all the melamine dissolved. To this was added 5.3 grams of o-toluidine and 60ml of concentrated hydrochloric acid as catalyst and the reaction mixture was heated at 95˙C under reflux conditions for about 4 hours and 45 minutes with continuous stirring. The reaction mixture gelled into a brown hard mass in about 4 hours 5 minutes. 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 24 hours. The brown transparent hard mass was crushed to proper mesh size and the sieved resin was stored for further experimental work.

5. Properties of ion exchange resins

(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 density: The wet absolute density of the free base form of the anion exchangers and amphoteric exchangers was determined by the conventional method described by Kunin. Results are reported in Table.

(3) 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 1 N NaCl solution. The acid consumed (neutralised) after 24 hours was determined by titrating aliquot of the solution with standard alkali. Blank readings were obtained by keeping separately 0.5gram of the ion exchanger in the free base form with 50ml of distilled water and determining the free alkalinity, if any. Blank readings were considered while calculating the capacity per gram of absolute dry resin.

(4) pH titration curve: .05 gram of the resins MUF, MAF and MOTF 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 bank and the supertant solution, the capacities of the resins at different pH values were calculated (moisture content was taken into account).

(5)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 were opened and the weighed bottles with the sample and the lids were then transferred to desiccator containing CCl_4 . The contents were allowed to equilibriate in CCl_4 for certain hours. The desiccator lid was then removed and the weighing bottle were covered as rapidly as possible. The bottle with samples were then reweighed. The pore volume was calculated from the gain in weight of the samples recorded.

(6)Thermal stability: 1 gram of the resin was placed in a glass ampoule with 20ml 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 distil 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. Thus, the quantity of acid or alkali liberated during heat treatment was determined.

(7)Rate of exchange:

$OH^{-} \rightarrow Cl^{-}$ Exchange

0.5gram of the free base form of the resins were 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 realised at different time intervals was calculated.

(8)Storage and Conditioning: The ion exchange resins after synthesis may contain low molecular weight polymers or unreacted monomers. In order to remove these materials Soxhlet extraction was adopted using Soxhlet apparatus with appropriate solvents. Solvents used for this purpose were ethyl alcohol and acetone. The anion-exchange resins MUF, MAF and MOTF were first extracted with acetone and then with ethyl alcohol. The solvent extracted resins were conditioned by alternate treatment with 4% sodium hydroxide and 5% hydrochloric acid. After several alternate exhaustion and regeneration cycles, the resins were thoroughly washed free of acid or alkali and were dried until free flowing and stored in tightly stoppered bottles. Anion exchange resins while regenerating in “Chloride” form were washed free of acid with alcohol and stored in tightly stoppered bottles. Synthesis of Anion-exchange resins Melamine was used as cross-linking agent for the synthesis of the resins.

(9)Result Table: Three ion exchange resins were prepared and only indigenously available raw materials such as urea, aniline, o-toluidine, and melamine were used. The nature of the raw materials leaves no choice but to adopt condensation polymerization for the synthesis of the resins. Concentrated hydrochloric acid were used as catalyst in the synthesis of anion exchange resins. The reaction time of MAF is less than MUF and MOTF.

Physicochemical Properties of Resins: Results of physicochemical properties are reported in the following table.

1) Properties of ion exchange resins

No.	**Name**	**Moisture content %**	**Wet absolute density**	**Total capacity meq/gm of absolute dry resin**	**Pore volume ml/gm in the free base form**
1	MUF	15.0	3.1 gm /ml	1.76	0.28
2	MAF	12.0	2.8	2.25	0.30
3	MOTF	12.6	4.6	2.85	0.25

2) p^H titration study of MUF in the free base form in the presence of 1.0N NaCl:

No.	**Volume of NaCl ml**	**Volume of HCl in NaCl ml**	**Equilibrium p^H**	**Capacity meq/gm of absolute dry resin**
1	00.0	50.0	0.901	2.000
2	22.5	27.5	1.15	1.800
3	30.0	20.0	1.379	1.500
4	42.5	07.5	1.750	1.200
5	47.5	02.5	2.200	0.900

3) p^H titration study of MAF in the free base form in the presence of 1.0N NaCl :

No.	**Volume of NaCl ml**	**Volume of HCl in NaCl ml**	**Equilibrium p^H**	**Capacity meq/gm of absolute dry resin**
1	00.0	50.0	0.856	2.158
2	12.5	37.5	0.981	1.874
3	27.5	22.5	1.010	1.700
4	42.5	07.5	1.500	1.200
5	47.5	02.5	2.410	0.600

4) p^{H} titration study of MOTF in the free base form in the presence of 1.0N NaCl:

No.	Volume of NaCl ml	Volume of HCl in NaCl ml	Equilibrium p^{H}	Capacity meq/gm of absolute dry resin
1	00.0	50.0	0.806	2.850
2	12.5	37.5	0.908	2.800
3	37.5	12.5	1.151	2.450
4	42.5	07.5	1.800	1.700
5	47.5	02.5	2.600	0.990

5) Thermal stability of resin

Temperature	Name	Capacity meq/gm of absolute dry resin	% loss in capacity of resin as determind after heating (in the free base form)	% loss in capacity of resin as determind after regeneration (in the free base form)
$80^{\cdot}$ C	MUF	1.76	1.78	1.76
	MAF	2.25	2.25	2.21
	MOTF	2.85	2.95	2.85
$100^{\cdot}$ C	MUF	1.76	1.78	1.76
	MAF	2.25	2.25	2.21
	MOTF	2.85	2.95	2.85
$120^{\cdot}$ C	MUF	1.76	1.78	1.35
	MAF	2.25	2.25	2.21
	MOTF	2.85	2.95	1.94

6. Conclusion

Three resins were synthesized and characterised. During the course of the investigation reported here only indigenously available raw material were used. Properties of the resins such as capacity, wet absolute density, porosity and p^{H} titration curves were studied by the conventional methods as adopted for various ion- exchange reins. The result showed that the anion – exchange resins were functioning as weak base anion exchangers.

From the porosity value, it is revealed that
MAF>MUF>MOTF

Data in the table 4 revealed that the synthesized anion exchangers could be used safely upto $80^{\cdot}$C. Above $80^{\cdot}$C these resins were susceptible to temperature resulting in lowering in capacity.

Thermal stability of the anion exchangers in the hydroxyl and chloride form was in the following order,
MAF>MUF>MOTF

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. Theoretical elemental contents of the resins were calculated from the moles of the reactants taken for the synthesis and the observed capacity of the resins. These values were compared with the elemental content experimentally determined and were found to be almost similar.

Physicochemical Properties of Resins Results of physicochemical properties are reported in Table 1-3.

Determinations of moisture contents Anion-exchange resins: About 1 gram of the air-dried resin in the free base form was accurately 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. Results are reported in Table 1. Determination of density the wet absolute density of the free base form of the anion exchangers and amphoteric exchangers was determined by the conventional method described by Kunin. Results are reported in Table 1.

References

1.Benesi, H.A., Bonner, R.U. and Lee C.P. (1965). Anal. Chem.
2.Carleton, Ellis (1935). The Chemistry of synthetic resins
3.Dharkar, K.P., Khamborkar A.K.and Kalambe A.B. Res J. (2012). Chem. Sci., vol-2 (12)
4.Gosh, Pranab, Das Tapan, Res J. (2011). Chem. Sci.,1(3),18-25
5.Gzing, (2013). Monatshefte fur chemie –chemical monthly -144,1369
6.Helfferich, F., (1962). Ion-Exchange, McGraw-Hill Book Inc., New York
7.Krishnaswamy, N. and Dasare, B.D., J. 411 (1962). Sci. and Ress., 21D,12,438
8.Kunin, R., (1952). Ion-Exchange Resin, John Wiley and Sons, inc., New York
9.Masram, D. K Kariya; N Bhave. (2007). Epolymers, (2007), 75, 1618-7229
10. Zagorodni, AA. (2007). Ion Exchange Materials: Properties And Applications: Elsevier, Amsterdam, 496.