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Studies for Ion Exchange Capacities of Some Zirconium-Based Exchangers

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ABSTRACT

Inorganic ion exchangers- Zirconium Succino Arsenate, Phthalo Arsenate, and Anthralo Arsenate have been prepared from Zirconyl Nitrate solution, Sodium Arsenate and organic acids i.e. Succinic, Phthalic and Anthralic acid, in 1:1:1 molecular ratio. To prove the ion exchanging capabilities of the prepared compound, it is customary to determine their exchanging capacities under different conditions, its cation exchange capacities have been studied as a function of pH. The difference in limiting and total capacities of these compounds shows that the ionizable groups are mostly acidic and they have their utility only at higher pH of the solution. The highest exchange capacity has been observed for the exchangers at pH between 10-11in the presence of 10% NaCl.

INTRODUCTION

After the discovery of fact that the insoluble compound obtained from Zirconium salts and phosphoric acid can be used separate uranium and plutonium from fission products (1, 2). Zirconium phosphate becomes a model ion exchanger. The stability of this compound towards ionizing radiation, high temperature, and many common chemical reagents has made an important product which is of great use chemical processing contaminated moderator or cooling in atomic reactor. To improve its ion exchanging properties a (3) tried to prepare exchanger of citric acid, similarly, phthalic an hydride used to prepare zirconium phthalophosphate (4), similar to zirconium phosphate, arsenate, tungstate, or molybdate has also been prepared. some zirconium-based exchangers have been reported (5-9), In this zirconium arsenate has been taken in place of phosphate, due to conditions of preparation for zirconium arsenate are similar to those of zirconium phosphate (10,11). Carboxylic acid, phthalic acid is used to prepare the proposed exchanger, Abbreviation used for Zirconium Phthalo Arsenate, ZrPthAs. Introduction of some acidic group in the zirconium arsenate and thus some zirconium-based three-component ion exchanger has been prepared. Bi-functional cation exchanger, Zirconium Phthalo Arsenate, ZrPthAs have been prepared from Zirconyl nitrate, Sodium Arsenate, and phthallic acid in different molecular ratios.

The property which characterizes a polymer as an exchanger is the number of groups that it possesses to bring about the exchange reaction. This property can be measured as milliequivalents of exchangeable ions per gram of the dry polymer or exchanger. One can also determine these groups by their ionization studies in solution as weekly or highly dissociated acids or bases. The determination of total exchange capacity is not as simple as it appears. it depends on several factors:

i. The low rates of exchange.
ii. Un-favourable exchange equilibrium between certain pairs of ions.
iii. Inaccessibility of certain exchange sites.
iv. Instability of some exchange polymers. Equilibrium pH titrations help in getting the information regarding the exchanging groups in the polymer.
   These titrations need the setting up of experiments with samples of the exchangers in contact with varying amounts of the ions to be exchanged.

EXPERIMENTAL

1. Procedure for determining the limiting exchange capacities of the prepared exchangers :
Take 50 ml of Normal $BaCl_2$ solution in 150 ml in three flasks each with stopper .0.25 gm of the exchanger was used to determine this capacity under equilibrium conditions. The required amount (0.25 gm) of the exchanger was then added to each such flask. The solution was then given swirling motion to bring the solid and the solution was left as such for

24 hrs. After this aliquots were withdrawn from each flask and estimated for acid generation by titrating it against 0.01N NaOH solution. A similar batch study was carried out with a normal NaCl solution.

2. Procedure for determining the total exchange capacities of the prepared exchangers in alkaline solution:
1.00 gm of the exchanger was taken in a 500 ml Erlenmeyer flask. An electrolyte solution containing 5% NaCl and NaOH sufficient to give its 0.1N solution in deionized water was used for exchange purposes. The solution was standardized properly strength in the mixture.200 ml of this solution was added to the exchanger kept in the Erlenmeyer flask. It was left for 48 hrs, after 48 hrs 50 ml aliquots of the supernatant liquid were titrated with standard 0.1 N HCl using phenolphthalein as an indicator and calculate exchange capacity. A similar procedure was adopted for the remaining two exchangers. To observe the effect of salt concentration on the exchange capacities, a similar method was used with 1% and 10% NaCl in an electrolyte solution containing 0.1 N NaOH. The pH of such solutions was noted by a pH meter and it was ~11.

3. Procedure for capacity determination by limiting exchange method at different pH:
0.25 gm of the exchanger was equilibrated with 50 ml of the electrolyte solution containing NaCl to provide 1.0 N solution and sufficient buffering material to maintain the required pH of the experiment. Such solution was equilibrated for ~ 48 hrs. After equilibration, the supernatant liquid was analyzed for the generated acidity due to the exchange of sodium ions.

As the solutions were also acidic initially hence the separate electrolytes samples were prepared in the same manner and estimated their content. The difference in acidity after the exchange was taken equivalent to the H^+ generated due to exchange at the pH of the solution. A similar method was used at different pH to observe the effect of pH on the exchange capacities of the new exchangers.

RESULT AND DISCUSSION

The limiting exchange capacities of different exchangers have shown a maximum capacity of ~0.78 meq/gm for ZrSAs.The use of an electrolyte of uni and divalent metal ion does not make much difference in the exchange capacities (Table-1 & Figure-1).

The total capacities of inorganic exchangers prepared here show quite high value in presence of NaOH. At pH (10-11) The total capacities are again very high for ZrSAs and ZrPthAs.But it is clear from the data. The presence of salt and its concentration is very important for these exchangers. the total capacity of ZrSAs exchanger from6.00to 6.7 meq for change of NaCl concentration from 1 to 10%,it is 3.96meq/gm at 1% NaCl 6.84 meq/gm at % NaCl and 7.35 meq/gm at 10% NaCl for ZrPthAs. At pH 10-11 the value of exchange capacity is highest for ZrPthAs, 7.35 meq/gm dry resins, 6.7 meq/gm for ZrSAs, and 5.524 meq/gm for ZrAnAs. Thus all the exchangers show the value of quite high order in alkaline solutions. (Table-2 & Figure-2).

The effect of the acidic and alkaline medium is clear from exchange capacity data at different pH values (Table-3 & Figure-3).

Table-1: Limiting Exchange capacities of the Exchangers(Heated up to 100°C)

Medium	Limiting Exchange Capacities meq/gm Exchanger		
	ZrSAs	**ZrPthAS**	**ZrAnAs**
Neutral $BaCl_2$ (N) Solution	0.78	0.56	0.40
Neutral NaCl (N) Solution	0.76	0.56	0.40

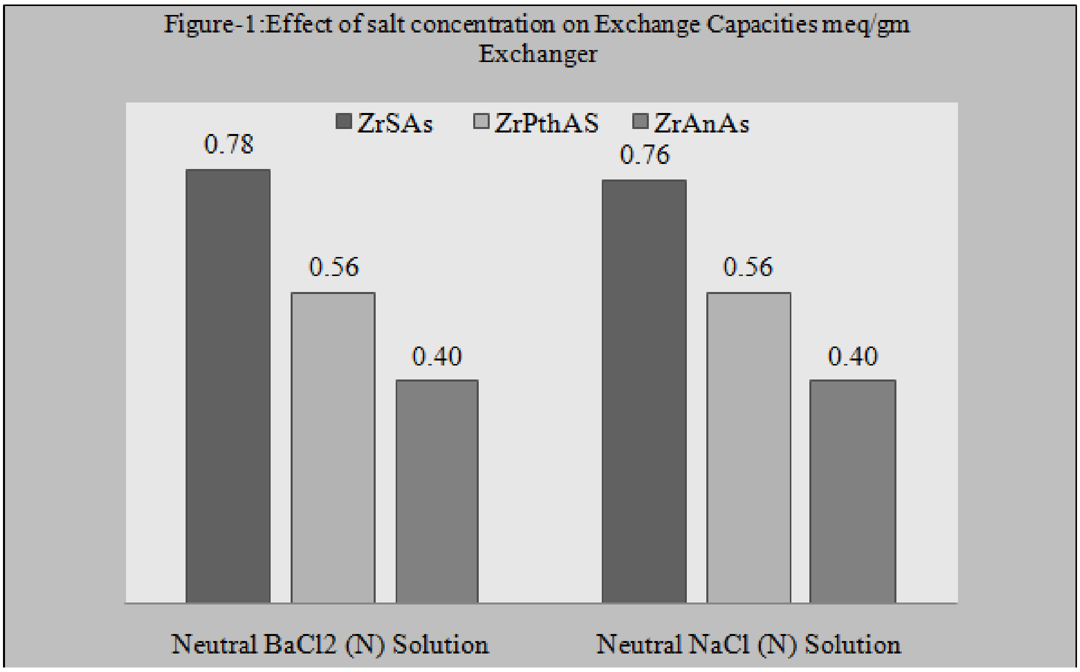


Table-2: Total Exchange capacities of the Exchangers (In alkaline medium)				
pH	Salt %	Total Exchange Capacities meq/gm Exchanger		
		ZrSAs	ZrPthAS	ZrAnAs
10-11	1	6.00	3.96	3.600
10-11	5	6.48	6.84	5.040
10-11	10	6.70	7.35	5.524

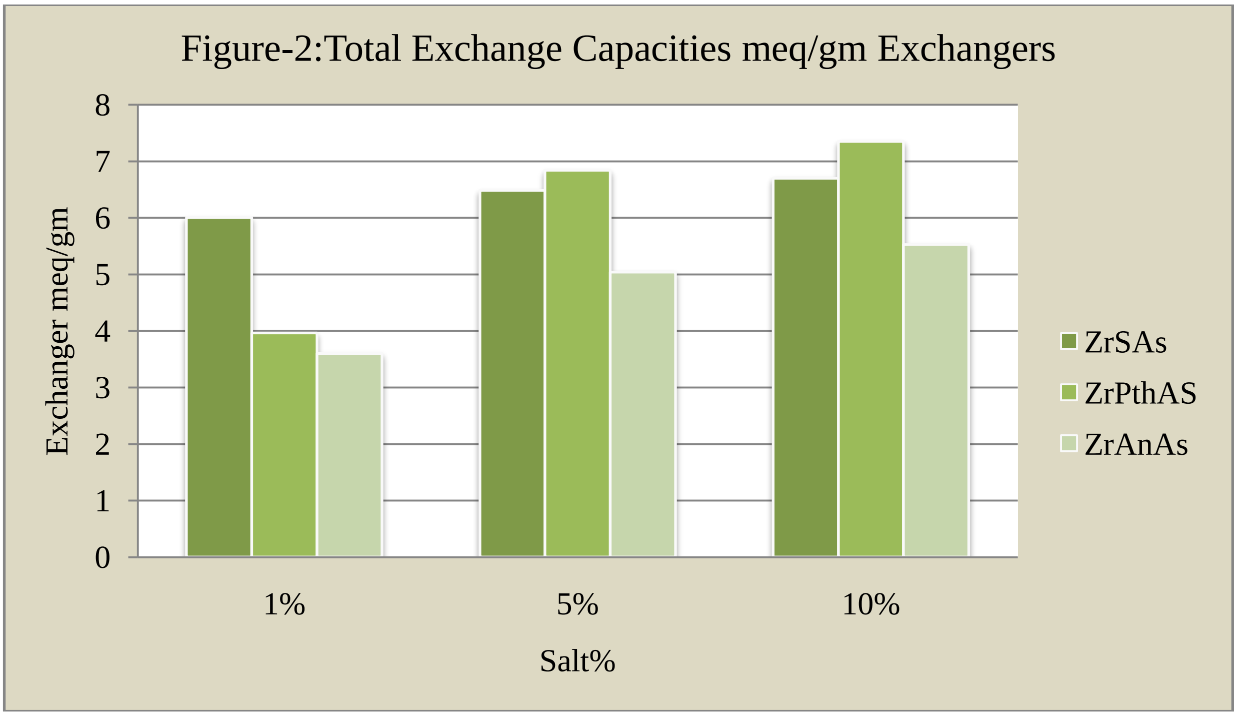
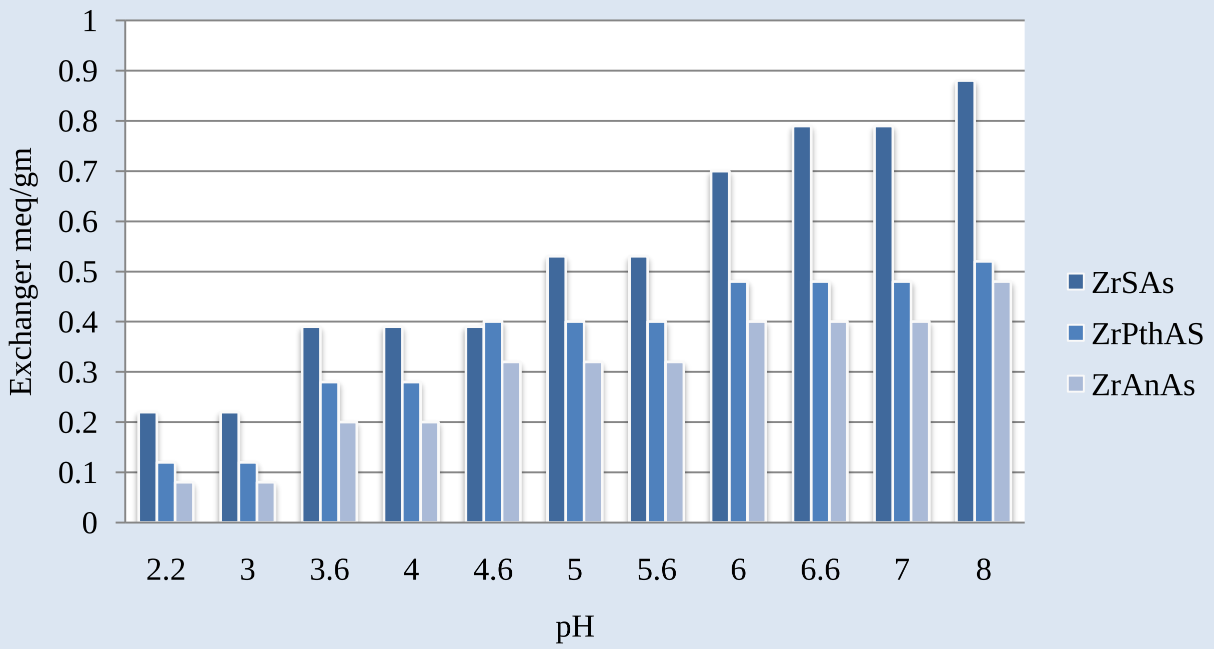


Table-3: Effect of pH on Limiting Exchange capacities of the Exchangers

pH	Salt %	Limiting Exchange Capacities meq/gm Exchanger		
		ZrSAs	**ZrPthAS**	**ZrAnAs**
2.2	5	0.22	0.12	0.08
3.0	5	0.22	0.12	0.08
3.6	5	0.39	0.28	0.20
4.0	5	0.39	0.28	0.20
4.6	5	0.39	0.40	0.32
5.0	5	0.53	0.40	0.32
5.6	5	0.53	0.40	0.32
6.0	5	0.70	0.48	0.40
6.6	5	0.79	0.48	0.40
7.0	5	0.79	0.48	0.40
8.0	5	0.88	0.52	0.48

Figure-3:Effect of pH



CONCLUSION

1. The nature of ions is not very important for exchanging capacities.

2. ` Increase in exchange capacity with an increase in salt concentration has been seen in ZrPthas and ZrAnAs.
3. The highest exchange capacity has been observed for these exchangers at pH 10-11 in presence of 10% NaCl solution. A gradual increase in capacity with increasing pH is a general conclusion.

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