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STUDY ON ION EXCHANGE BEHAVIOR OF AUCHLITEARA9366 AND AUCHLITEA378 RESINS CHEMICALLY DEGRADED IN PERCHLORIC ACID MEDIUM

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ABSTRACT

The resins AuchliteARA-9366 and AuchliteA-378 in chloride form were degraded by treating with 0.005 M and 0.01M $HClO_4$ for 24 h under continuous magnetic stirring. The degraded resins in chloride form were equilibrated separately with bromide and iodide ion solutions of different concentrations in the temperature range of 30.0 - 45.0 ^oC for 3 h. the equilibrium constants (*K*) values forCl^-/I^- and Cl^-/Br^- ion exchange reactions were calculated. The results indicate that during Cl^-/I^- reaction with rise in temperature the *K* values decreases from 4.59x 10^{-2} to 3.44x 10^{-2} for resin AuchliteARA-9366 degraded using 0.005 M $HClO_4$medium which was lower than the decrease in *K* values from 4.61 x 10^{-2} to 3.74 x 10^{-2} observed for the resin AuchliteARA-9366 degraded using 0.01M $HClO_4$ medium. Similar results were obtained for Cl^-/Br^-ion exchange reaction. Forresin AuchliteA-378 during Cl^-/I^- reaction the *K* values decreases from 5.83 x 10^{-2} to 4.14 x 10^{-2} for AuchliteA-378 degraded in 0.005 M $HClO_4$ medium which was lower than the decrease in *K* values from 6.04 x 10^{-2} to 4.09 x 10^{-2} observed for the resin AuchliteA-378 degraded using 0.01M $HClO_4$ medium. Similar results were obtained for Cl^-/Br^- ion exchange reaction. The decrease in *K* values with rise in temperature indicate exothermic ion exchange reactions which was supported by negative standard enthalpy (ΔH^0) and standard entropy(ΔS^0) values obtained during the two ion exchange reactions carried out by using both the resins AuchliteARA-9366 and AuchliteA-378. The thermodynamic data obtained here was used to predict the performance suitability of the chemically degraded nuclear grade strong base and industrial grade weak base resins in perchloric acid medium.

Keywords: *nuclear and industrial grade resin;performance stability; AuchliteARA9366 and Auchlite A-378;* $HClO_4$ *degradation.*

I. INTRODUCTION

Ion exchange technology was used in many industrial applications involving purification and separationsand has been applied in nuclear fuelcycle operations and other activities for the treatment of radioactive liquids[1].For the removal of specific radionuclides Inorganic ion exchange materials play an important role while the useorganic ion exchange resins continueglobally for the separation and purification of ion exchange waste[2]. No theoretical data was available for understanding how they function, or the parameters that affectson the performance of a resin for a particular application [3].This article covers perchloric acid degradation effect on the ion-exchange reactions, ion selectivity, hardness leakageandpercholoric acid degradation effecton the ion exchange capacity of resin. Considering the extensive industrial applications of ion exchange materials in the present study attempts were made to evaluate the performance of perchloric acid degradedAuchliteARA-9366 and AuchliteA-378 resins[4-9]. The resins AuchliteARA-9366 was a strong base nuclear grade anion exchange resinhaving cross-linked polystyrene matrix while The resins AuchliteA-378 is weakly basic industrial grade anion exchange resinhaving macro porouscross-linked polystyrene matrix[10].The surface morphology of resin was studied by scanning electron microscopy (SEM), the chemical degradation of resins in perchloric acid medium was characterized with the help of Fourier Transform Infrared Spectroscopy (FTIR) [11]. Thermal studies of the resins were carried out to determine their mode of decomposition, entropy change (ΔS), free energy change (ΔG) and enthalpy change (ΔH).

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II. METHOD & MATERIAL

Materials

The ion exchange resin AuchliteARA-9366 and AuchliteA-378 as supplied by the manufacturer (Auchtel Products Ltd., Mumbai, India) are the anion exchangers in hydroxide form. The details regarding various physico-chemical properties of the two ion exchange resins are presented in Table.1

Table 1.Physico-chemical properties of anion exchange resins

Ionexchange resin	Matrix	Functional Group	Mean particleSize(mm)	Moisture Content (%)	Operatingp H	Maximumoperat ing temperature(°C)
AuchliteARA9366	Polystyrene	quaternary ammonium	0.3-1.0	50	0-14	60.0
AuchliteA-378	Polystyrene	tertiary ammonium	0.3-1.2	48	0-7	60.0

Chemical degradation of resins

In order to understand the performance of chemically degraded resins, in the present study the AuchliteARA-9366 and AuchliteA-378 resins are exposed to perchloricacid ($HClO_4$) degradation. In order to bring about perchloricacid ($HClO_4$)degradation, 25g of the resins in chloride form are transferred separately in 100mL round bottom flask containing 50mL of 0.005M $HClO_4$ and 0.01M $HClO_4$and the mixture was continuously stirred on the magnetic stirrer for 24h. The ished chemically degraded resins in chloride form are air dried over P_2O_5 in desiccators and used for further studies.

Conditioning and equilibration of chemically degraded resins in perchloric acid medium

The conversion of the Resins in chloride form was done by using 10% potassium chloride solution in a conditioning Column by usual Methods [12]. The soluble impurities of the resin are removed by repeated soxhlet extraction using water and occasionally with distilled methanol. The perchloricacid(0.005M $HClO_4$ and 0.01M $HClO_4$) degraded resins in chloride form are equilibrated separately for 3h with bromide ion solutions of different concentration from 0.01M,0.025M,0.05M,0.075M and 0.10M in the equilibration temperatures ranging from 30.0°C to 45.0°C as explained [13]. After 3h the resins were filtered and the bromide ion solutions in equilibrium with resins in chloride form are analyzed for their chloride and bromide ion concentrations potentiometrically by using standard 0.1M silver nitrate solution.

$$R\text{-}Cl + Br^-_{(aq)} \rightleftharpoons R\text{-}Br + Cl^-_{(aq)} \qquad (1)$$

From the results the equilibrium constants*K* for the reaction (1) is calculatedin the equilibration temperature ranging from 30.0°C to 45.0°C.

$$R\text{-}Cl + I^-_{(aq)} \rightleftharpoons R\text{-}I + Cl^-_{(aq)} \qquad (2)$$

Similar studies are performed to study the equilibrium constants*K* for the reaction (2) by equilibrating chemically degraded resins in chloride form with iodide ion solution of different concentrations from 0.01M,0.025M,0.05M,0.075M and 0.10Mfor 3h in the equilibration temperatureranging from 30.0°C to 45.0°C.

III. RESULTS AND DISCUSSION

The equilibrium constants (*K*) for reactions 1 and 2are calculated by the equation

$$K = \frac{C_{R\text{-}X} . C_{Cl^-}}{(A - C_{R\text{-}X}) . C_{X^-}} \qquad (3)$$

Here, R represent the resin phase; *A* is the ion exchange capacity of the resin; X^-represents $I^-$and Br^-ions. For different concentrations of X^-ions in solution at a given temperature, *K* values are calculated and an average of *K* for this set of experiment is obtained. Similar *K* values are calculated for the reactions 1 and 2 performed at different temperatures. From the slope of the graph of log *K* against 1/T (in Kelvin)[Figures 1 to 4] the enthalpies of the ion exchange reactions 1 and 2 are calculated. From the values of *K* at different temperatures, the standard enthalpy change ΔH^o (kJ.mol^{-1}), standard free energy change ΔG^o (kJ.mol^{-1}) and standard entropy change ΔS^o(kJ.K^{-1}mol^{-1}) values are calculated of the above uni-univalent ion exchange reactions. The values of equilibrium constant (K), ΔH^o,ΔG^o and ΔS^o for the above uni-univalent ion exchange reactions were also calculated for two resins subjected to perchloric acid degradation in 0.005M $HClO_4$ and 0.01M $HClO_4$ medium were presented in **Tables 2 to 5**

Table 2 Equilibrium constant for the ion exchange Reaction (1) and Reaction (2) using AuchliteARA-9366 resin degraded using 0.005M $HClO_4$.

Amount of the ion exchange resin in chloride form = 0.500 g, Ion exchange capacity = 1.74meq./0.5 g, Equilibration temperature = 30.0 ^oC.

AuchliteARA-9366 resin degraded using 0.005M $HClO_4$ Reaction (1)						AuchliteARA-9366 resin degraded 0.005M $HClO_4$. Reaction (2)					
Initial concentration Of bromide ions (M)	Final Conc. of bromide ions (M) C_{Br^-}	Change in bromide ion conc.	Conc. of Cl^- ions exchanged (M) C_{Cl^-}	Amount of bromide ions Exchange on the resin meq./0.5 g C_{RBr}	Equilibrium constant K x10^{-2}	Initial concentration of iodide ion (M)	Final Conc. Of iodide ions (M) C_{I^-}	Change in iodide ion Conc.	Conc. Of Cl^- ions exchanged (M) C_{Cl^-}	Amount of iodide ions exchanged on the resin meq./0.5 g C_{RI}	Equilibrium constant K x10^{-2}
0.01	0.0064	0.0036	0.0036	0.18	10.93	0.01	0.0046	0.0054	0.0054	0.27	99.18
0.025	0.0196	0.0054	0.0054	0.27	6.88	0.025	0.018	0.007	0.007	0.35	14.68
0.05	0.0448	0.0052	0.0052	0.26	2.52	0.05	0.0414	0.0086	0.0086	0.43	8.87
0.075	0.0696	0.0054	0.0054	0.27	1.49	0.075	0.0638	0.0112	0.0112	0.56	8.46
0.1	0.0946	0.0054	0.0054	0.27	1.14	0.1	0.0886	0.0114	0.0114	0.57	6.72
Average *K*					**4.59**	**Average *K***					**27.58**

Table 3 Equilibrium constant for the ion exchange Reaction (1) and Reaction (2) using AuchliteA-378 resin degraded using 0.005M $HClO_4$.

Amount of the ion exchange resin in chloride form = 0.500 g, Ion exchange capacity = 2.104meq./0.5 g, Equilibration temperature = 30.0 ^oC.

AuchliteA-378 resin degraded using 0.005M $HClO_4$. Reaction (1)						AuchliteA-378 resin degraded using 0.005M $HClO_4$. Reaction (2)					
Initial concentration Of bromide ions (M)	Final Conc. of bromide ions (M) C_{Br^-}	Change in bromide ion conc.	Conc. of Cl^- ions exchanged (M) C_{Cl^-}	Amount of bromide ions Exchange on the resin meq./0.5 g C_{RBr}	Equilibrium constant K x10^{-2}	Initial concentration of iodide ion (M)	Final Conc. Of iodide ions (M) C_{I^-}	Change in iodide ion Conc.	Conc. Of Cl^- ions exchanged (M) C_{Cl^-}	Amount of iodide ions exchanged on the resin meq./0.5 g C_{RI}	Equilibrium constant K x10^{-2}
0.01	0.0048	0.0052	0.0052	0.26	18.32	0.01	0.0033	0.0067	0.0067	0.335	84.58
0.025	0.019	0.006	0.006	0.3	6.47	0.025	0.0166	0.0084	0.0084	0.42	18.37
0.05	0.0444	0.0056	0.0056	0.28	2.25	0.05	0.0406	0.0094	0.0094	0.47	8.34
0.075	0.0696	0.0054	0.0054	0.27	1.19	0.075	0.0666	0.0084	0.0084	0.42	3.19
0.1	0.0946	0.0054	0.0054	0.27	0.91	0.1	0.0916	0.0084	0.0084	0.42	2.44
Average *K*					**5.83**	**Average *K***					**23.39**

Table 4 Thermodynamics of ion exchange reactions AuchliteARA-9366 andAuchliteA-378 resin degraded using 0.005M $HClO_4$.

$$R\text{-}Cl + Br^-_{(aq)} \rightleftharpoons R\text{-}Br + Cl^-_{(aq)} \qquad (1)$$

$$R\text{-}Cl + I^-_{(aq)} \rightleftharpoons R\text{-}I + Cl^-_{(aq)} \qquad (2)$$

Ion exchange resin AuchliteARA-9366 degraded using 0.005M $HClO_4$									Ion exchange resin AuchliteA-378 degraded using 0.005M $HClO_4$								
Equilibration temperature (^oC)	Equilibrium Constant K x10^{-2}		ΔH^o ($kJ.mol^{-1}$)		ΔG^o ($kJ.mol^{-1}$)		ΔS^o ($kJ.K^{-1}mol^{-1}$)		Equilibration temperature (^oC)	Equilibrium Constant K x10^{-2}		ΔH^o ($kJ.mol^{-1}$)		ΔG^o ($kJ.mol^{-1}$)		ΔS^o ($kJ.K^{-1}mol^{-1}$)	
	Reaction		Reaction		Reaction					Reaction		Reaction		Reaction		Reaction	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)		(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
30	4.59	27.5							30	5.	23.						

		8								83	39						
35	3.53	27.30	-14.03	-12.57	8.48	3.56	-0.071	-0.051	35	4.42	21.88	-17.37	-4.84	7.94	3.90	-0.080	-0.027
40	3.52	24.34							40	4.21	21.67						
45	3.44	22.04							45	4.14	21.22						

Table 5 Thermodynamics of ion exchange reactions using AuchliteARA-9366 and AuchliteA-378 degraded using 0.01M $HClO_4$.

$$R\text{-}Cl + Br^-_{(aq)} \rightleftharpoons R\text{-}Br + Cl^-_{(aq)} \qquad (1)$$

$$R\text{-}Cl + I^-_{(aq)} \rightleftharpoons R\text{-}I + Cl^-_{(aq)} \qquad (2)$$

Ion exchange resin AuchliteARA-9366 degraded using 0.01M $HClO_4$.									Ion exchange resin AuchliteA-378 degraded using 0.01M $HClO_4$.								
Equilibration temperature (°C)	Equilibrium Constant K x10^{-2}		ΔH° (kJ.mol^{-1})		ΔG° (kJ.mol^{-1})		ΔS° (kJ.K^{-1}mol^{-1})		Equilibration temperature (°C)	Equilibrium Constant K x10^{-2}		ΔH° (kJ.mol^{-1})		ΔG° (kJ.mol^{-1})		ΔS° (kJ.K^{-1}mol^{-1})	
	Reaction		Reaction		Reaction					Reaction		Reaction		Reaction		Reaction	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)		(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
30	4.61	27.87	-12.29	-17.76	8.19	3.95	-0.06	-0.07	30	6.04	26.61	-23.58	-19.82	7.70	4.11	-0.09	-0.07
35	4.51	25.96							35	6.00	19.48						
40	3.93	19.71							40	4.44	18.31						
45	3.73	19.56							45	4.08	18.04						

The equilibrium constant *(K)* values forCl^-/I^- andCl^-/Br^- ion exchange reactions using AuchliteARA-9366 resins degraded in 0.005M $HClO_4$medium decreases from 27.59x10^{-2} to 22.04x10^{-2} and from 4.60x10^{-2} to 3.44x10^{-2} respectively with rise in equilibration temperature from 30.0 °C to 45.0 °C. The standard enthalpy change (ΔH°) and standard entropy change (ΔS°) calculated for Cl^-/I^- ion exchange reactions are -12.57kJ.mol^{-1}and -0.05kJ.K^{-1}mol^{-1} respectively which are higher than the respective values of -14.03kJ.mol^{-1} and -0.07kJ.K^{-1} mol^{-1} as that obtained for Cl^-/Br^- ion exchange reactions. However, low value of standard free energy change **(**ΔG°) 3.56kJ.mol^{-1}is obtained for Cl^-/I^- ion exchange reactions as compared to 8.48kJ.mol^{-1} obtained for Cl^-/Br^- ion exchange reactions **(Table 4)**.

The equilibrium constant *(K)* values forCl^-/I^- andCl^-/Br^- ion exchange reactions using AuchliteA-378 resins degraded in 0.005M $HClO_4$medium decreases from 23.39x10^{-2} to 21.22x10^{-2} and from 5.83x10^{-2} to 4.14x10^{-2} respectively with rise in equilibration temperature from 30.0 °C to 45.0 °C. The standard enthalpy change (ΔH°) and standard entropy change (ΔS°) calculated for Cl^-/I^- ion exchange reactions are -4.85kJ.mol^{-1}and -0.03kJ.K^{-1}mol^{-1} respectively which are higher than the respective values of -17.37kJ.mol^{-1} and -0.08kJ.K^{-1} mol^{-1} as that obtained for Cl^-/Br^- ion exchange reactions. However, low value of standard free energy change **(**ΔG^o)3.91kJ.mol^{-1} is obtained for Cl^-/I^- ion exchange reactions as compared to 7.95kJ.mol^{-1} obtained for Cl^-/Br^- ion exchange reactions **(Table 4)**.

The equilibrium constant (*K)* values forCl^-/I^- andCl^-/Br^- ion exchange reactions using AuchliteARA-9366 resins degraded in in 0.01M $HClO_4$medium decreases from 27.87x10^{-2} to 19.56x 10^{-2} and from 4.61x10^{-2} to 3.74 x10^{-2} respectively with rise in equilibration temperature from 30.0 ^oC to 45.0 ^oC. The standard enthalpy change (ΔH^o), standard free energy change (ΔG^o) and standard entropy change (ΔS^o) calculated for Cl^-/I^- ion exchange reactions are -17.76kJ.mol^{-1}, 3.95kJ.mol^{-1}and -0.07kJ.K^{-1}mol^{-1} respectively which are lower than the respective values of -12.29kJ.mol^{-1},8.20kJ.mol^{-1} and -0.06 kJ.K^{-1}mol^{-1} as that obtained for Cl^-/Br^- ion exchange reactions **(Table 5)**.
The equilibrium constant (*K)* values forCl^-/I^- andCl^-/Br^- ion exchange reactions using AuchliteA-378 resins degraded in 0.01M $HClO_4$medium decreases from 26.61x10^{-2} to 18.04x10^{-2} and from 6.04x10^{-2} to 4.09x10^{-2} respectively with rise in equilibration temperature from 30.0 ^oC to 45.0 ^oC. The standard enthalpy change (ΔH^o) and standard entropy change (ΔS^o) calculated for Cl^-/I^- ion exchange reactions are -19.82kJ.mol^{-1}and -0.08kJ.K^{-1}mol^{-1} respectively which are higher than the respective values of-23.59kJ.mol^{-1} and -0.10kJ.K^{-1} mol^{-1} as that obtained for Cl^-/Br^- ion exchange reactions. However, low value of standard free energy change **(**ΔG^o) 4.11kJ.mol^{-1}is obtained for Cl^-/I^- ion exchange as compared to 7.71kJ.mol^{-1} obtained for Cl^-/Br^- ion exchange reactions **(Table 5)**.
The high *K* values obtained for Cl^-/I^-ion exchange reactions as compared to the Cl^-/Br^- ion exchange reaction for both the resins indicate their greater selectivity for iodide ions in the solution as compared to that of bromide ions which is also supported by the standard free energy change (ΔG^o), standard entropy change (ΔS^o) and standard enthalpy change (ΔH^o) values as given in **Tables4 & Table5**.

The equilibrium constant(K) values for both Cl^-/I^- and Cl^-/Br^- ion exchange reactions were slightly increases but nearly half of the equilibrium constants(K) values obtained for fresh resin AuchliteARA-9366 with rise in concentration of $HClO_4$ medium from 0.005M to 0.01M which indicates that the resin AuchliteARA-9366 mildly oxidized in perchloric medium which were also seen in the SEM micrograph and FTIR spectrum of the resin AuchliteARA-9366. But in case of AuchliteA-378 resin, The equilibrium constant (K) values obtained for both Cl^-/I^- and Cl^-/Br^- ion exchange reactions were nearly doubled than the equilibrium constant (K) values obtained for the fresh resin AuchliteA-378 indicating that both Cl^-/I^- and Cl^-/Br^- ion exchange reactions more feasible with rise in the concentration of perchloric acid medium from 0.005M to 0.01M than the fresh resin AuchliteA-378.

Graphs

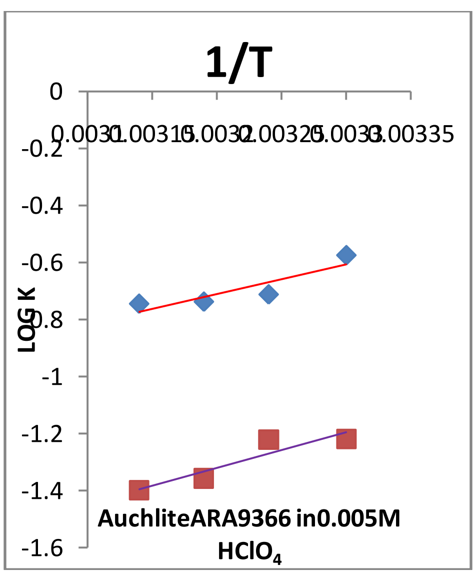

Figure 1ShowsVariation of equilibrium constant with temperature for AuchliteARA-9366 for Cl^-/I^- and Cl^-/Br^- ion exchange reaction using 0.005M$HClO_4$

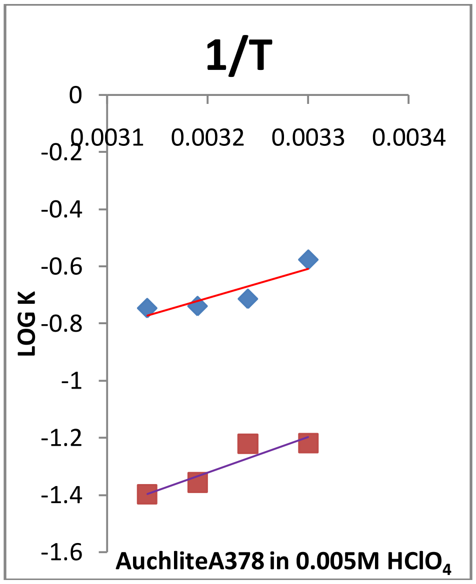

Figure 2 Shows Variation of equilibrium constant with temperature for AuchliteA378 for Cl^-/I^- and Cl^-/Br^- ion exchange reactionusing 0.005M$HClO_4$..

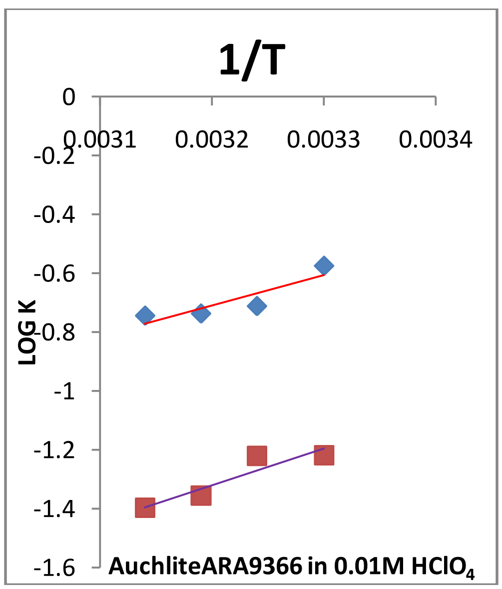

Figure 3ShowsVariation of equilibrium constant with temperature for AuchliteARA9366 forCl^-/I^- and Cl^-/Br^-ion exchange reactionusing 0.01M$HClO_4$..

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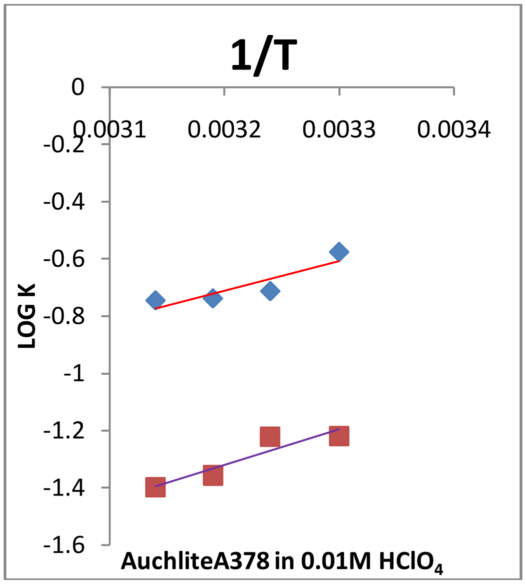

Figure 4ShowsVariation of equilibrium constant with temperature for AuchliteA-378 for Cl⁻/I⁻ and Cl⁻/Br⁻ ion exchange reaction using 0.01MHClO$_4$

FTIR spectrum of fresh and chemically degraded AuchliteARA-9366 resin using perchloric acid.

FTIR spectra (in 4000–450 cm^{-1}range) of fresh as well as perchloric acid degraded samples of AuchliteARA-9366 and AuchliteA-378 resins. The spectra are recorded in KBr pellets (2 mg resin/ 200 mg KBr) using a FTIR PerkinElmer 1750 spectrophotometer. The chemical degradation effect on the two resins is studied by comparing the FTIR spectra of fresh resin with that of degraded resins[14-19].In the FTIR spectrum of fresh resin(Figure 5) AuchliteARA-9366, the sharp strong broad band is observed at 3366 cm^{-1} corresponding to the signal vibration of O-H bond of the water or the quaternary ammonium group (R_4-N^+). The sharp band between1380-1349 cm^{-1}is for -C-N stretching while a variable absorption bands between 1633-1614cm^{-1} is due to the stretching vibrations of –C=C- of alkenes group. The weak band at 3031cm^{-1} is the characteristic stretching band for aromatic ring. A moderate band at 2925cm^{-1} is due to the C-H stretching band for –CH_2 group. A moderate and sharp band at 1416cm^{-1} and 1470cm^{-1} is due to the –C-H bending bands for - CH_2 group. The variable band at1511cm^{-1} is the –C=C- stretching for aromatic ring, the sharp band at 828cm^{-1} and moderate band at 705cm^{-1} is the characteristic bands of p-substituted and o-substituted aromatic rings.Figures 6 and 7 are the FTIR spectrum of AuchliteARA-9366 resin chemically degraded using 0.005M and 0.01M percholoric acid ($HClO_4$). On comparing the IR spectra of the fresh resin (figure 5) and the IR spectra of resin degraded using 0.005M $HClO_4$ (figure 6)it is observed that the characteristic –C-N stretching band at 1349cm^{-1} disappears in the IR spectrum.Also the IR spectra of resin degraded using 0.01M $HClO_4$ (figure 7)the characteristic –C-N stretching band in the region of 1380-1349 cm^{-1}and -C-H stretching band at 3031cm^{-1} for aromatic ring are completely disappeared. This clearly indicates that quaternary ammonium groups undergo oxidation with 0.01M $HClO_4$acid medium and there is no significant change in structure of the resin, but with rise in the concentration perchloric acid some of the resin sites were blocked or cracked for the ion exchange reaction which can be also seen in the scanning electron micrograph of the resin in SEM images (figures 12 and 13).

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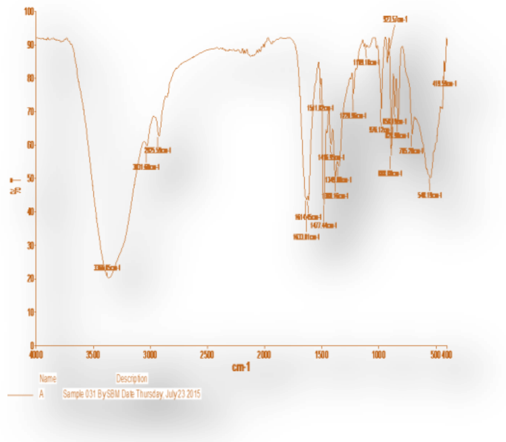

Figure 5

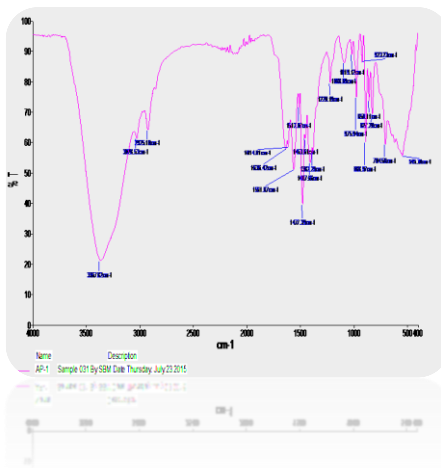

Figure 6

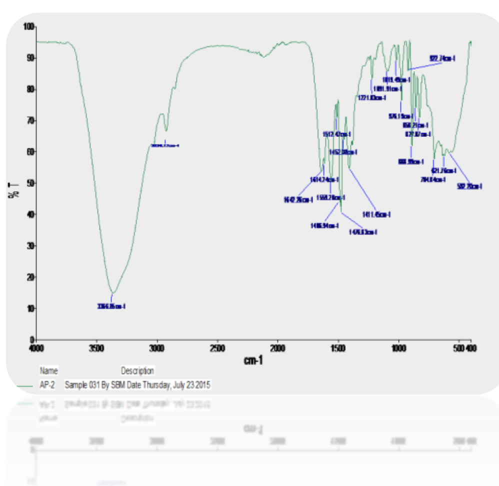

Figure 7

Figure 5-7. FTIR Spectrum of fresh resin, chemically degraded in 0.005M $HClO_4$and 0.01M $HClO_4$ medium AuchliteARA-9366.

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FTIR spectrumoffresh and chemically degraded AuchliteA-378resin using perchloric acid.

In the IR spectrum(Figure 8.) of fresh AuchliteA-378 resin the sharp and strong broad band appears at 3418cm^{-1} is for the amine salts group and bands appears in the region 2854-2703cm^{-1}are of -N-H stretching in amine salts(R_3-N^+-H). The strong band at 1168cm^{-1} is for -C-N stretching in aliphatic amine and the weak band at1369 cm^{-1}is for -C-N stretching in aromatic amines. A variable absorption band at 1614 cm^{-1} is for –C=C- stretching for alkenes group. The weak band at 3022cm^{-1} is the characteristic stretching band for aromatic ring. A strong band at 2926cm^{-1}and weak band at 2854cm^{-1} is the C-H stretching band for –CH_2 group. A moderate and sharp band at 1475cm^{-1}and1426cm^{-1}are due to the –C-H bending vibrations in -CH_2 group. The moderate band at1511cm^{-1}is due to the –C=C- stretching in aromatic ring. The strong band at 704cm^{-1} is the characteristic band of mono substituted aromatic rings.

Figures 9 and 10are the FTIR spectra's of AuchliteA-378 resin degraded in 0.005M and 0.01M $HClO_4$. It was observed that the characteristic –C-N stretching band at 1369cm^{-1}nearly disappears in the IR spectrum of 0.005M $HClO_4$medium (figure 9) which indicates that the resin is slightly oxidized in $HClO_4$acid medium. From the FTIR spectrum of perchloric acid degraded resin it can be conclude that the resin is oxidized in the perchloric acid medium and there is no significant change in structure of the resin and but only some of the resin sites are blocked or cracked for the ion exchange reaction with rise in the concentration of acid degradation medium which is also confirmed by comparing the SEM images of fresh resin (figure 14) and degraded resin in perchloric acid medium of different concentrations (figures 15 to 18).

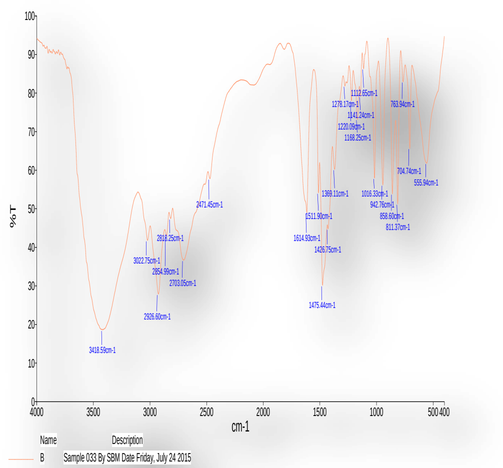

Figure 8

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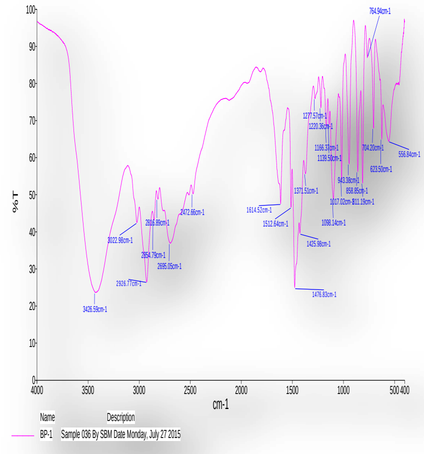


Figure 9

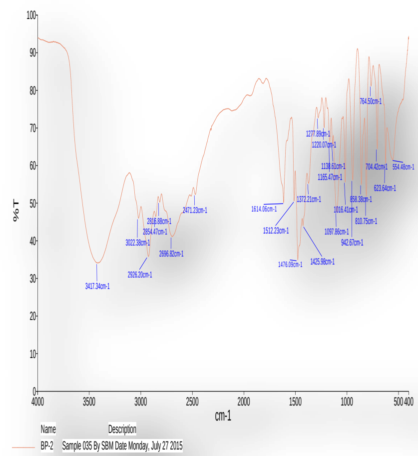


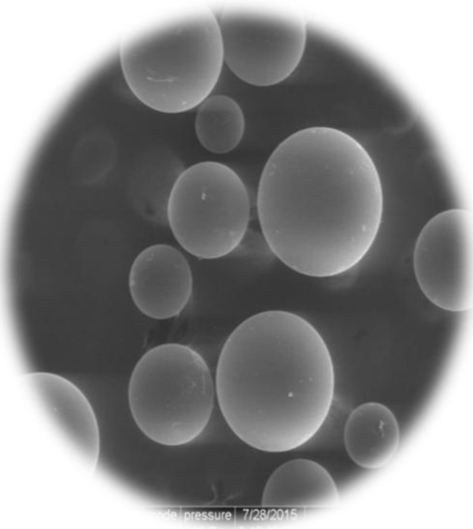
Figure 10

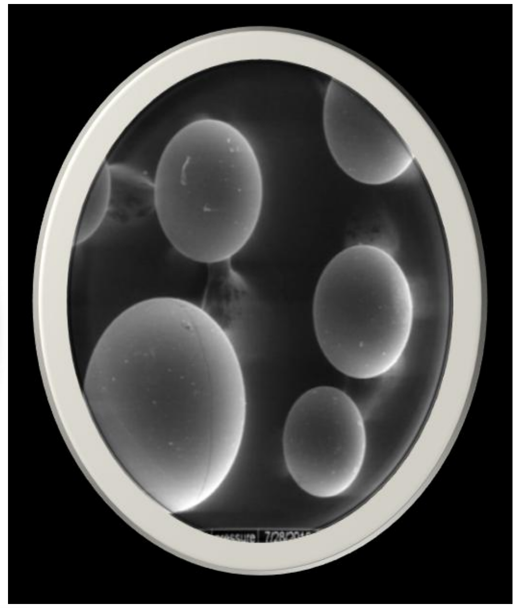
Figure 8-10. FTIR Spectrum of fresh resin chemically degraded in 0.005M $HClO_4$and 0.01M $HClO_4$ medium AuchliteA-378.

Scanning electron microscopy (SEM) studies of fresh (at room temperature) and chemically degraded resin using 0.005M $HClO_4$&0.01M $HClO_4$AuchliteARA-9366 resin.

Scanning electron micrographs of both fresh and degraded resin surfaces are obtained with the help of SEM technique using JSM-6380LA Scanning Electron Microscope (Jeol Ltd., Japan). The powders are precisely fixed on an aluminum sub layer using double-sided graphite tape and then are made electrically conductive by coating in a vacuum with a thin layer of carbon, for 30 seconds and at 30 W. The pictures are taken at an excitation voltage of 15 kV under a 90 Pascal pressure and a magnification of x150, x500, x1000,x 2500 and ×5000.

The SEM image of fresh ion exchange resins AuchliteARA-9366 is taken to examine its surface morphology [20-21].Figure 11 shows its plane spherical structure having smooth surface. In the scanning electron micrograph of chemically degraded resin AuchliteARA-9366 by using 0.005M $HClO_4$shows large cracks on the plane spherical surface of the resin and indicates that the resin may be mildly oxidized in the percholoric acid medium (Figure 12). The surface of the resin is appearing too rougher in the percholoric acidic medium as compare to that of fresh resin (Figure 11).similarly the SEM of AuchliteARA-9366 in 0.01M $HClO_4$ medium shows large cracks and thread like appearance on the plane spherical surface of the resin giving an indication about oxidation of resin in the percholoric acid medium (Figure 13). The roughness of resin surface still increases in the percholoric acidic medium as compare to that of fresh resin (Figure 11).





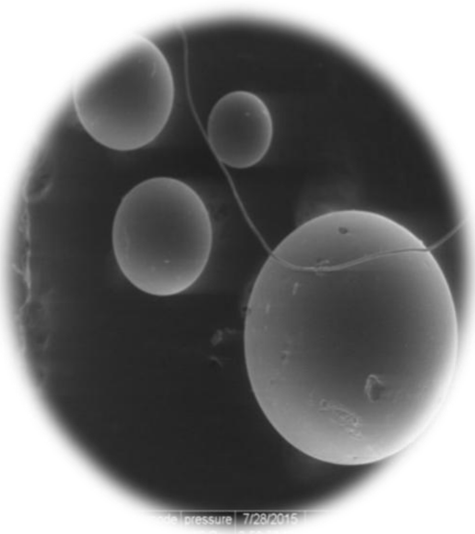
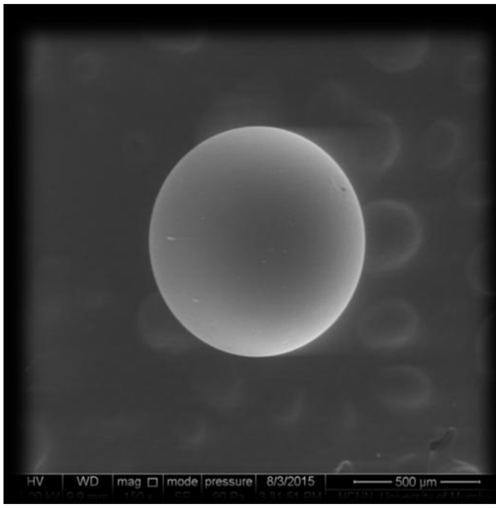


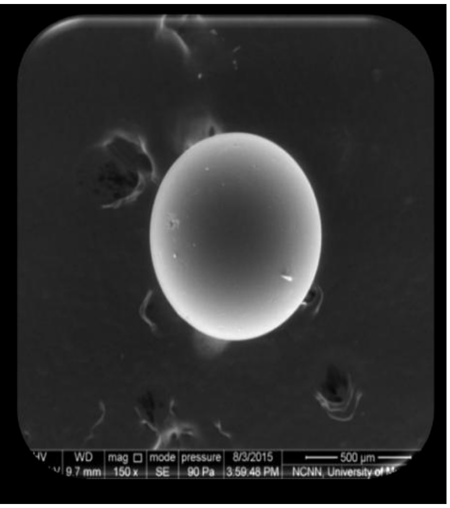
Figure 11SEM image of fresh AuchliteARA-9366.Figure 12SEM image of AuchliteARA-9366 resin Figure 13SEM image of AuchliteARA-9366 resin

Chemically degraded in 0.005M $HClO_4$.Chemicallydegraded using 0.01M $HClO_4$.

Scanning electron microscopy (SEM) studies of fresh (at room temperature) and chemically degraded AuchliteA-378 resin using 0.005M $HClO_4$&0.01M $HClO_4$

The SEM images of AuchliteA-378 resin chemically degraded by using 0.005M $HClO_4$shows large cracks on the plane spherical surface of the resin which is due to the mild oxidation of resin in the percholoric acid medium (Figures 15-18). The surface of the resin is appearing too rougher in the percholoric acidic medium as compare to that of fresh resin (Figure 14).The SEM images of AuchliteA-378 in 0.01M $HClO_4$ medium (Figures 17 and 18) shows still large cracks and thread like appearance on the plane spherical surface of the resin as compared to that observed in the SEM images of resin degraded in 0.005M $HClO_4$ medium (Figures 15-16). This indicates that the oxidation in percholoric acid medium is more pronounced with rise in concentration. The roughness of the resin surface increases with increase in the concentration of percholoric acidic as observed by comparing the SEM images of degraded resin (Figure 15-18) with that of fresh resin (Figure 14).





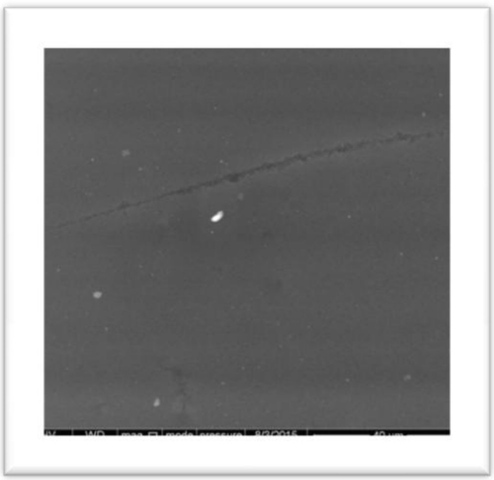
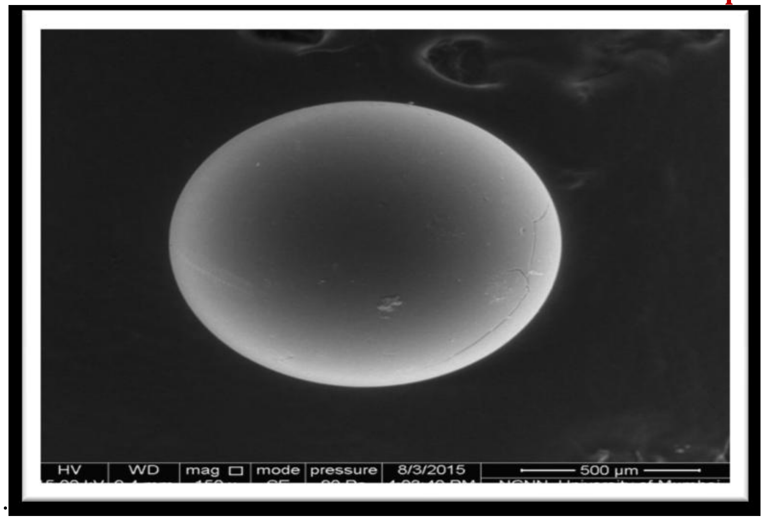


Figure 14.SEM image of fresh Figure15. SEM of AuchliteA-378 in 0.005M $HClO_4$ Figure 16.SEM of AuchliteA-378 in 0.005M $HClO_4$
AuchliteA-378 resin.Image at x150 magnification Image at x2500 magnification



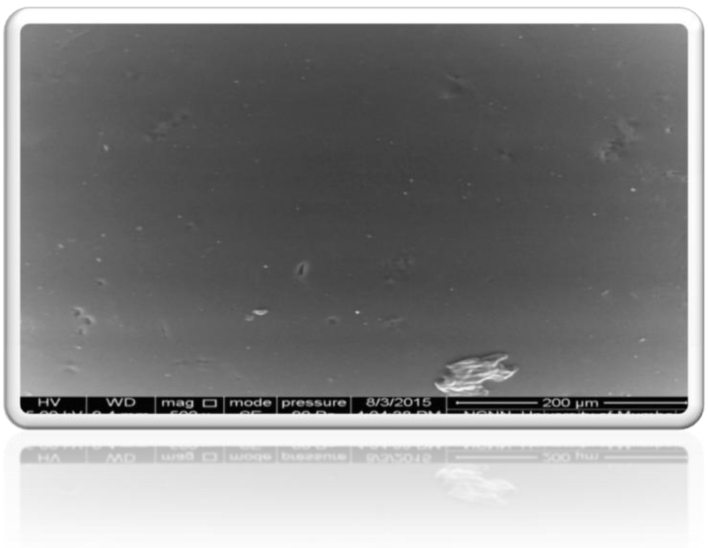


Figure 17 SEM of AuchliteA-378 in 0.01M $HClO_4$.Figure 18SEM of AuchliteA-378 in 0.01M $HClO_4$
Image at x150 magnification Image at x500 magnification

IV. CONCLUSION

The present investigation will be useful for understanding the degradation effect of various oxidizing and reducing agents on the performance and selectivity behavior various industrial and nuclear grade resin materials for treatment of waste water effluents. The results and data obtained from such research investigation will be helpful in selecting the particular ion exchange resins for efficient industrial applications and will be useful in optimization of process parameters to achieve the maximal efficiency of the ion exchange material.

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