Research Article

THE STUDY OF THERMAL DEGRADATION EFFECT ON THE SELECTIVITY BEHAVIOUR OF NUCLEAR GRADE RESIN DUOLITEARA9366

Patange AN*

Department of Chemistry, Bhavan's College, Munshi Nagar, Andheri (West), Mumbai, Maharashtra 400058

ARTICLE INFO	ABSTRACT
	The effect of thermal degradation on the equilibrium constant (K) and enthalpy values for the ion exchange reactions were carried out at different temperatures to predict the selectivity behaviour of ion exchange resins DuoliteARA-9366 towards iodide and bromide ions in solution. The resin was thermally degraded at different degradation temperatures of 70.0°C, 100.0°C and 120.0°C. The experiment was extended further by performing the above ion exchange reaction using thermally degraded ion exchange resins DuoliteARA-9366. The standard enthalpy values of the above ion exchange reaction performed by using fresh and degradedresins DuoliteARA-9366 at 70.0°C, 100.0°C and 120.0°C were calculated as-47.87,-18.79, -9.50, -15.63 kJ/mole for Cl^-/I^- and for Cl^-/Br^- were -14.77,-4.71,-10.89,-6.84 kJ/mole respectively. The thermodynamic data obtained here reveal that iodide ions were more selective towards the resin surface compared to bromide ions. Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the resins degradation steps.

INTRODUCTION

The selection of appropriate ion exchangers depends on the needs of the system (Wiley *et al*, 1997) and the process of selection becomes more difficult at high concentrations for chemically similar ions in the waste water. In the past decade inorganic ion exchange materials have a good alternative for replacement or complement for conventional organic ion exchange resins. Because of specific physical and chemical reasons the use of organic ion exchange resins is continued globally for various technical applications (Baumann *et al*, 1960) and cannot be replaced by inorganic ion exchangers (Patange *et al*, 2014). The synthetic organic ion exchange resins having many industrial applications like purification and separations (Singare *et al*, 2014 and Patange, *et al*, 2014) and were mainly used for water treatment and preparation of demineralized water (Lokhande *et al 2008 and* Hatsis *et al, 2001*). The resins used must be resistant to degradation effect and should exhibit consistent performance (Bhargava *et al*, 1997) under various degradation conditions. In view of this, the present research work was carried out to understand the performance of the anion exchange resins namely Duolite ARA-9366 (nuclear grade) exposed to thermal degradation at different degradation temperatures of 70.0°C, 100.0°C and 120.0°C (McNeill *et al*,1995). The performance behaviour of

the thermally degraded resinswas evaluated by studying their selectivity behaviour towards bromide and iodide ions in the solution and also by studying the thermodynamic feasibility of the ion exchange reactions. Therefore, in the present investigation thermal degradation of resin (Decker *et al 1999, and* Santhiya *et al*, 1999) was performed to understand the degradation steps and to compare the relative thermal stability.

MATERIALS AND METHODS

Materials

The ion exchange resin Duolite ARA-9366 as supplied by the manufacturer (Auchtel Products Ltd.Mumbai, India) are the anion exchangers in hydroxide form. The physico-chemical properties of the ion exchange resins were represented in Table1

Thermal degradation of resins

In order to understand the performance of thermally degraded resins, in the present study 25g of DuoliteARA-9366 resin in chloride form were taken in watch glass and in oven separately at 70.0°C, 100.0°C and 120.0°C temperature for 24 h. After 24h, the thermally degraded resin is cooled over P_2O_5in desiccators.

Corresponding author: **Patange AN**
Department of Chemistry, Bhavan's College, Munshi Nagar, Andheri (West), Mumbai, Maharashtra 400058

**Table 1** Physico-chemical properties of anion exchange resins

Ionexchangeresin	Matrix	Functional Group	Mean particleSize(mm)	Moisture Content (%)	Operating pH	Maximumoperating temperature(°C)
DuoliteARA9366	Polystyrene	quaternary ammonium	0.3-1.08	50	0-14	60.0

Conditioning and equilibration of thermally degraded resins

The conversion of the Resins in chloride form was done by using15% KCl solution in a conditioning Column by regular Methods (Kaczmarek *et al*, 2008). The soluble impurities of the resin are removed by repeated soxhlet extraction using water and occasionally with distilled methanol to remove the non-polymerized organic impurities. The thermally 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 (Jiang *et al*,1999). After 3h the resins were filtered and the bromide ion solutions in equilibrium with resins in chloride form are analysed for their chloride and bromide ion concentrations potentiometrically by using standard 0.01M AgNO₃solution.

$$D\text{-}Cl + Br^-_{(aq)} \rightleftharpoons D\text{-}Br + Cl^-_{(aq)} \qquad (1)$$
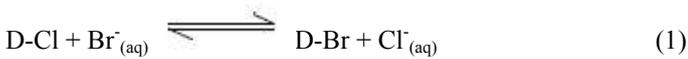
From the results the equilibrium constants *K* for the reaction (1) is calculated for different equilibration temperatures ranging from 30.0°C to 45.0°C.

$$D\text{-}Cl + I^-_{(aq)} \rightleftharpoons D\text{-}I + Cl^-_{(aq)} \qquad (2)$$
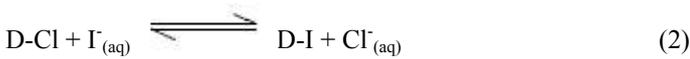
Similar studies are performed to study the equilibrium constants *K* for the reaction (2) by equilibrating thermally degraded resins in chloride form with iodide ion solution of different concentrations for 3h in the different equilibration temperature ranging from 30.0°C to 45.0°C.

RESULTS AND DISCUSSION

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

$$K = \frac{C_{D\text{-}X} \cdot C_{Cl^-}}{(B\text{-} C_{D\text{-}X}) \cdot C_{X^-}} \qquad (3)$$

Here, D represent the resin phase; *B* 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) the enthalpies of the ion exchange reactions 1 and 2 are calculated. From the values of *K* at different temperatures, the standard enthalpy change ΔHᵒ (kJ.mol⁻¹), standard free energy change ΔGᵒ (kJ.mol⁻¹) and standard entropy change ΔSᵒ(kJ.K⁻¹mol⁻¹) values are calculated of the above uni-univalent ion exchange reactions. The values of equilibrium constant (K), ΔHᵒ, ΔGᵒ and ΔSᵒ for the above uni-univalent ion exchange reactions were also calculated for two resins subjected to thermal degradation at 70.0°C,100.0°C and 120.0°C.

The thermodynamic parameters calculated for the ion exchange reactions 1 and 2 using the fresh resins and resins exposed to different degradation temperatures70.0°C, 100.0°C and 120.0°C.are presented in Tables 2 and 3.

The resins DuoliteARA-9366 degraded separately at higher temperatures of 70°C, 100°C and 120°C. The degraded resins are used to study the uni-univalent ion exchange reactions 1 and 2. It is observed that for both the Fresh and degraded resins the equilibrium constant (*K*) values calculated during Cl⁻/I⁻uni-univalent ion exchange reactions are higher than that obtained for Cl⁻/Br- uni-univalent ion exchange reaction under similar experimental conditions (Tables 2 to 3).The equilibrium constant (*K*) for both the uni-univalent ion exchange reactions decreases with rise in equilibration temperature resulting in exothermic reactions. The log *K* values are plotted against 1/T (in Kelvin), which gives a straight line graph with negative slope (Figures 1 to 4) from which the enthalpy values of the ion exchange reactions 1 and 2 are calculated. The equilibrium constant (*K)* values for Cl⁻/I⁻ and Cl⁻/Br⁻ uni-univalent ion exchange reactions using DuoliteARA-9366 resins degraded at 70°C decreases from 22.09x10⁻² to 16.35x10⁻² and from 5.07x10⁻² to 4.61x10⁻² respectively with rise in equilibration temperature from 30.0 °C to 45.0 °C.

Table 2 Equilibrium constant for the ion exchange Reaction (1) and Reaction (2) using DuoliteARA-9366 resindegraded at 70.0°C.

Amount of the ion exchange resin in chloride form = 0.500 g, Ion exchange capacity = 1.80meq./0.5 g, Equilibration temperature = 30.0 °C.

	DuoliteARA-9366 resin degraded at 70.0°C. Reaction (1)					DuoliteARA-9366 resin degraded at 70.0°C. Reaction (2)					
Initial conc. 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 ionsExchange on the resin meq./0.5 g C_{RBr}	Equilibr ium constant *K* x10⁻²	Initial conc. Of iodide ion(M)	Final Conc. Of iodide ions (M) C_{I^-}	Change in iodide ion Conc.	Conc. OfCl⁻ 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	0.0062	0.0038	0.0038	0.19	12.45	0.01	0.004	0.006	0.006	0.3	75.00
0.025	0.0196	0.0054	0.0054	0.27	7.21	0.025	0.017	0.008	0.008	0.4	19.37
0.05	0.0442	0.0058	0.0058	0.29	3.06	0.05	0.0408	0.0092	0.0092	0.46	9.74
0.075	0.0696	0.0054	0.0054	0.27	1.47	0.075	0.0672	0.0078	0.0078	0.39	3.52
0.1	0.0946	0.0054	0.0054	0.27	1.12	0.1	0.092	0.008	0.008	0.4	2.78
		Average *K*			5.06			Average *K*		22.08	Average *K*

Table 3 Thermodynamics of Cl⁻/Br⁻and Cl⁻/I⁻reactions using freshDuoliteARA-9366 and resin degraded at 70.0°C,100.0°C and 120.0°C.

Resin.	D-Cl + Br⁻(aq) ⇌ D-Br + Cl⁻(aq)		(I)				ΔH° (KJ/mol)	ΔG° (KJ/mol)	ΔS° (KJ/mol)
	D-Cl + I⁻(aq) ⇌ D-I + Cl⁻(aq)		(II)						
	Equilibrium Temperature (°C)		30	35	40	45	---	---	---
Fresh DuoliteARA-9366	Equilibrium Constant In K x10⁻²	Reaction (I)	8.15	6.60	6.46	6.06	-14.77	6.95	-0.07
		Reaction (II)	59.77	33.56	27.20	23.77	-47.87	2.82	-0.16
DuoliteARA-9366. Degraded at 70.0°C.	Equilibrium Constant In K x10⁻²	Reaction (I)	5.06	4.84	4.80	4.60	-4.71	7.82	-0.040
		Reaction (II)	22.08	21.68	16.51	16.35	-18.79	4.30	-0.074
DuoliteARA-9366. Degraded at 100.0°C	Equilibrium Constant In K x10⁻²	Reaction (I)	6.91	5.49	5.40	5.13	-10.89	7.39	-0.05
		Reaction (II)	30.76	27.66	26.44	25.82	-9.50	3.34	-0.04
DuoliteARA-9366. Degraded at 120.0°C	Equilibrium Constant In K x10⁻²	Reaction (I)	6.91	6.70	6.53	6.04	-6.84	7.04	-0.04
		Reaction (II)	51.19	40.33	39.43	37.31	-15.63	2.25	-0.05

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 -18.79kJ.mol⁻¹, 4.30kJ.mol⁻¹ and -0.07kJ.K⁻¹mol⁻¹ respectively which are lower than the respective values of -4.71kJ.mol⁻¹,7.82kJ.mol⁻¹ and -0.04 kJ.K⁻¹mol⁻¹ as that obtained for Cl⁻/Br⁻ ion exchange reactions (Table 3). The equilibrium constant (K) values for Cl⁻/I⁻ and Cl⁻/Br⁻ ion exchange reactions using DuoliteARA-9366 resins degraded at 100°C decreases from 30.76x10⁻² to 24.87x10⁻² and from 6.92x10⁻² to 5.14x10⁻² respectively with rise in equilibration temperature from 30.0 °C to 45.0 °C. The standard enthalpy change (ΔH^o) and standard entropy change (ΔS^o) calculated for Cl⁻/I⁻ ion exchange reactions are -9.50kJ.mol⁻¹ and -0.04 kJ.K⁻¹mol⁻¹respectively which are higher than the respective values of -10.89kJ.mol⁻¹ and -0.06 kJ.K⁻¹mol⁻¹as that obtained for Cl⁻/Br⁻ ion exchange reactions. However, lower value of standard free energy change (ΔG^o) 3.35 kJ.mol⁻¹is obtained for Cl⁻/I⁻ ion exchange reactions as compared to 7.40 kJ.mol⁻¹ obtained for Cl⁻/Br⁻ ion exchange reactions (Table 3). The equilibrium constant (K) values forCl⁻/I⁻ andCl⁻/Br⁻ ion exchange reactions using DuoliteARA-9366 resins degraded at 120°C decreases from 51.20x10⁻² to 37.32x10⁻² and from 6.92x10⁻² to 6.05x10⁻² respectively with rise in equilibration temperature from 30.0 °C to 45.0 °C.

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 -15.64 kJ.mol⁻¹, 2.26kJ.mol⁻¹ and -0.06kJ.K⁻¹mol⁻¹ respectively which are lower than the respective values of -6.84kJ.mol⁻¹,7.04kJ.mol⁻¹ and -0.04kJ.K⁻¹mol⁻¹ as that obtained for Cl⁻/Br⁻ ion exchange reactions (Table 3). The high K values and standard enthalpy change (ΔH^o), standard free energy change (ΔG^o) and standard entropy change (ΔS^o) values obtained for Cl⁻/I⁻ion exchange reactions as compared to the Cl⁻/Br⁻ ion exchange reaction for fresh and thermally degraded resin DuoliteARA-9366at 70°C,100°C and 120°C indicate their greater selectivity for iodide ions in the solution as compared to that of bromideions

FTIR of fresh (at room temperature) and thermally (at 70.0°C, 100.0°C and 120.0°C) degraded DuoliteARA-9366 resin

FTIR spectra of fresh as well as thermally degraded samples of DuoliteARA-9366 were recorded in KBr pellets using a FTIR PerkinElmer 1750 spectrophotometer. The degradation effect on the resins was studied by comparing the FTIR spectra of fresh resin with that of degraded resins.
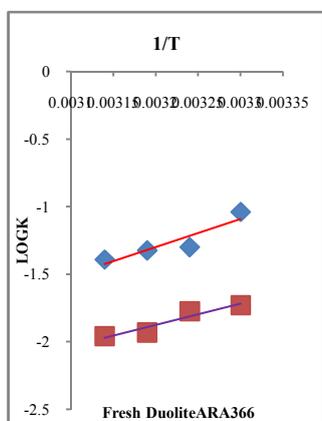

Figure 1 ShowsVariation of equilibrium constant with temperature for fresh DuoliteARA-9366for Cl⁻/I⁻ &Cl⁻/Br ⁻ ion exchange reaction..
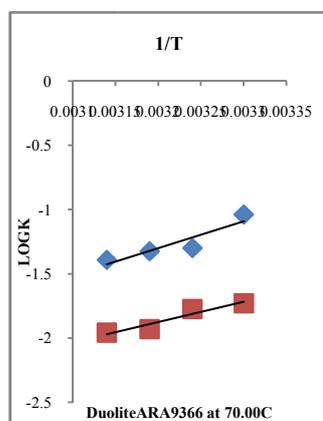
Figure 2 Shows Variation of equilibrium constant with temperature for fresh DuoliteARA-9366 forCl⁻/I⁻&Cl⁻/Br ⁻ ion exchange reaction degraded at 70°C.
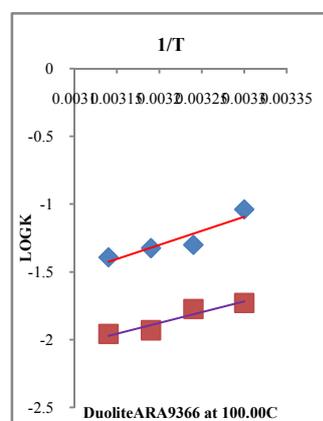
Figure 3 ShowsVariation of equilibrium constant with temperature for DuoliteARA-9366Cl⁻/I⁻&Cl⁻/Br ⁻ion exchange reactiondegraded **at 100°C.**
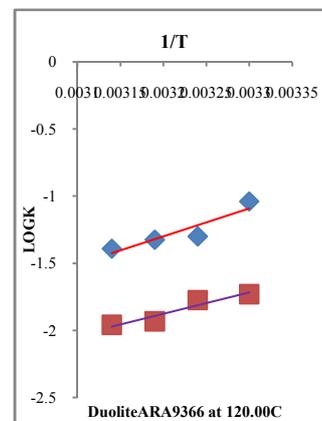
Figure 4 shows Variation of equilibrium constant with temperature for DuoliteARA-9366for Cl-/I-&Cl-/Br –ion exchange reactiondegraded at 120oC.
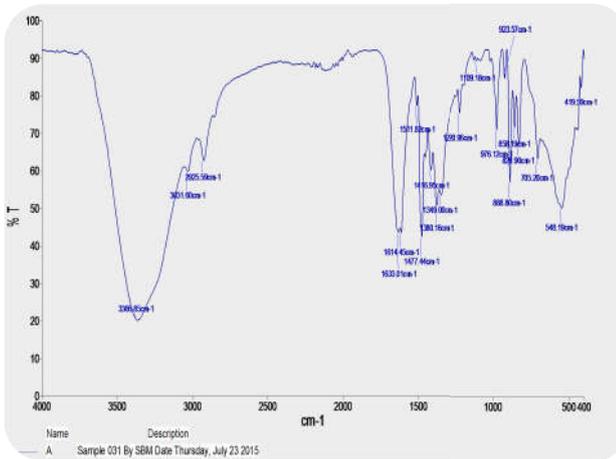
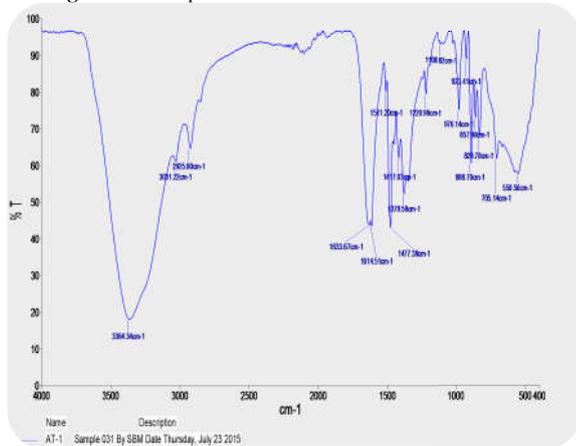**Figure 5** FTIR Spectrum of freshresin DuoliteARA-9366

Figure 6 FTIR Spectrum of degradedresin DuoliteARA-9366 at 70.0°C
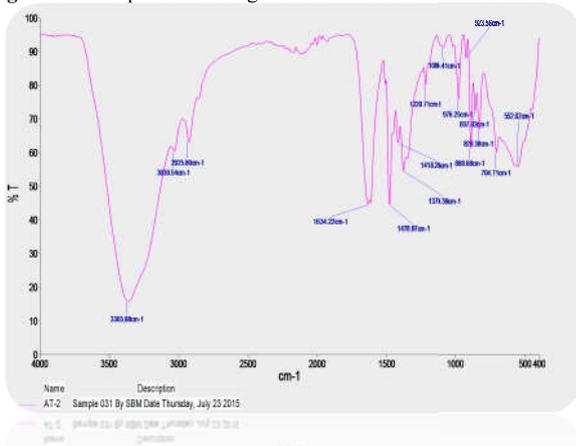

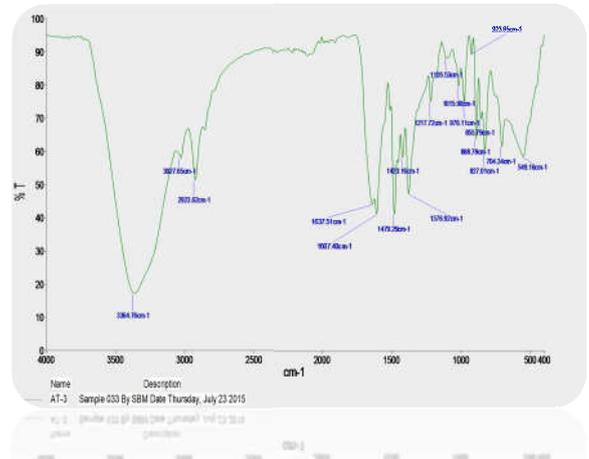**Figure 7** FTIR of degraded resin DuoliteARA-9366

Figure 8 FTIR of degraded resin DuoliteARA-9366 at 120.0°C

In the FTIR of fresh resin DuoliteARA-9366(Patange *et al*, 2017) (Figure 5), the sharp strong broad band is observed at 3366 cm^{-1}corresponding to the signal vibration of 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 to 8 are the FTIR spectrum of DuoliteARA-9366 resin thermally degraded at 70.0°C, 100.0°C and 120.0°C. It is observed that there were no significant changes in absorption frequencies of various characteristic absorption bands. The minor changes in the absorption frequencies might be due to the rise in degradation temperature from 70.0°C to 120.0°C. from IR spectra of the fresh resins (figure 5) and the spectrum of thermally degraded resin (figures 6 to 8) it can be seen that the resin was thermally stable and there was no significant change in structure of the resin, but only some of the sites of the resin were blocked or cracked for the ion exchange reaction with rise in the temperature which can be confirmed by comparing the SEM images (Patange *et al*, 2017)of fresh resin (figure 9) with that of thermally degraded resin (figures 10-12). Scanning electron microscopy (SEM) studies of fresh (at room temperature) and thermally (at 70.0°C, 100.0°C and 120.0°C) degraded DuoliteARA-9366 resin

Scanning electron micrographs of fresh and degraded resin surfaces were obtained with the help of SEM technique using JSM-6380LA Scanning Electron Microscope (Jeol Ltd., Japan). The pictures were taken at an excitation voltage of 15 kV under a 90 Pasca pressure and a magnification of x150, x500, x1000, x2500 and ×5000.
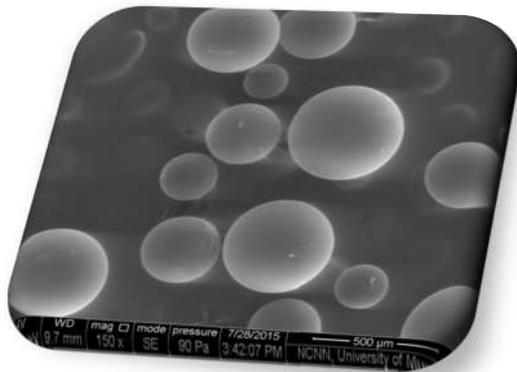
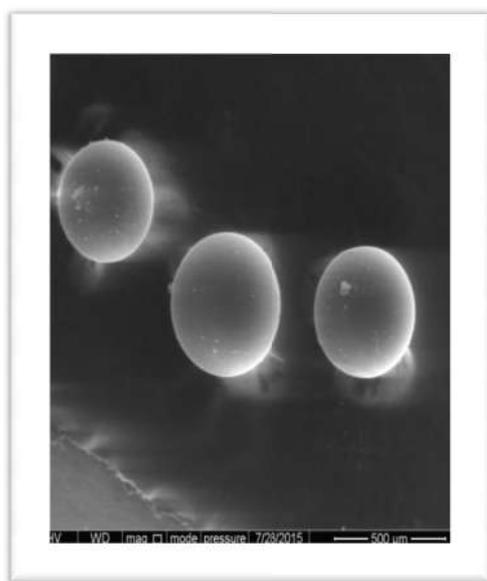**Figure 10** SEM of DuoliteARA-9366 at 100.0^{0}C
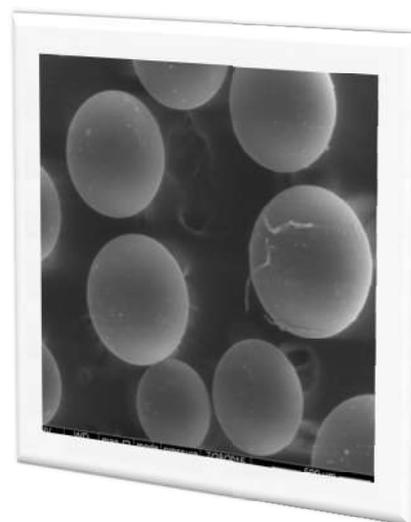

Figure 9 SEM of fresh DuoliteARA-9366.

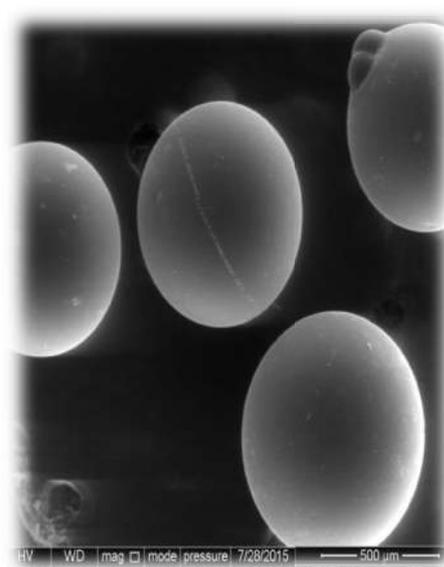**Figure 11** SEM of DuoliteARA-9366 at 100.0^{0}C

Figure 12 SEM of DuoliteARA-9366 at 120.0^{o}C

Figure 9 The SEM of fresh resins DuoliteARA-9366 (Patange *et al*, 2017) shows its plane spherical structure with smooth surface. In the scanning electron micrograph of thermally degraded resin DuoliteARA-9366at 70°C shows little cracks and thread like appearance on the surface of the resin (Figure 10). Similarly SEM of DuoliteARA-9366 at 100°Cshows little hair cracks and thread like appearance on the surface of the resin (Figure 11) and with rise in degradation temperature, the roughness of resin surface further increases Whereas the SEM (Figure 12) of resin at 120°C indicates that the cracks on the surface become sharper and the plane spherical surface of the resin gets deformed with rise in temperature. It was also seen that with rise in temperature the resin surface become rougher as compared to that of fresh resin.

CONCLUSION

The results of such studies will help in selection of proper ion exchange resins for effective industrial applications. The thermodynamic data obtained from the study will be helpful in optimization of process parameters to achieve the maximal efficiency of the ion exchange material.

References

1. Wiley J, and sons (1997). *Inc. J.Applpolym Sci.*, (64):1161-1167.
2. Baumann E,(1960) *J. Chem. and Eng. Data*, *5* : 376 .
3. Singare P, Patange A (2014) *International Letters of Chemistry, Physics and Astronomy*, *11*: 67.
4. Singare P, Patange, A(2014) *International Letters of Chemistry, Physics and Astronomy, 11* : 44 5Singare P , Patange, A(2014); *International Letters of Chemistry, Physics and Astronom*y, *6*
5. Lokhande, R, Singare,P (2008); *J .Porous Mater, ,15,*: 253 .
6. Hatsis,P. , Lucy, C (2001); *J. Chromatogr.*, 920A : 3
7. Bhargava, A., Janardanan, C (1997).; *Indian J.Chem., 36A*: 624 .
8. McNeill,I, Mohammed, M.H.(1995); *Polym. Degrad. Stab.*, *48*: 175 .
9. Decker, C, Zahouily, K. (1999); *Polym. Degrad. Stab.*, *64*: 293 .
10. Santhiya, D., Subramanian, S., Natarajan, K.A, Malghan, S. (1999); *J. Colloid. Int. Sci.*, *216*:143.

11. Kaczmarek, H., Felczak, A., Szalla, A.(2008*); Polym. Degrad. Stab., 93*:1259.
12. Jiang, D., Yao, Q.; McKinney, M., Wilkie, C (1999); *Polym. Degrad. Stab.*, *63*:423.
13. Patange, A., Singare P. (2017); *Research journal of pharmaceutical, biological and chemical sciences*,8(2):1866-1879
14. Patange, A (2017), *Orient. J. Chem.* 33(1):430-438.
15. Patange, A(*2017), Global Journal of engineering science and researches*,4(8)*:57-71*

How to cite this article:

Patange AN.2017, The Study of Thermal Degradation Effect on The Selectivity Behaviour of Nuclear Grade Resin Duoliteara9366. *Int J Recent Sci Res.* 8(9), pp. 20025-20030. DOI: http://dx.doi.org/10.24327/ijrsr.2017.0809.0811

****