Asian Journal of Chemistry; Vol. 29, No. 1 (2017), 209-212

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2017.20379

Effect of Resin Structure and Resin Fixed Ion on Selectivity of Perchlorate and Nitrate in Aqueous and Mixed Media†

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Received: 1 June 2016; *Accepted*: 4 October 2016; *Published online*: 29 October 2016; AJC-18129

The anion exchange of perchlorate and nitrate against chloride was investigated at different temperatures on weak base anion exchangers in aqueous and mixed media. The selectivity sequence observed for the resin Tulsion A-10X (MP) having acrylic matrix with polyamine group is $NO_3^- > ClO_4^- > Cl^-$ and for polystyrene based Amberlyst A-21 (MP) and Tulsion A-23 (Gel) having tertiary and quaternary ammonium groups respectively is $ClO_4^- > NO_3^- > Cl^-$. The study reveals that nitrate is more preferred than perchlorate on the resin having polyamine group. However the resins having tertiary and quaternary ammonium groups prefer perchlorate over nitrate. It is also observed that there is effect of temperature and solvent on selectivity of perchlorate and nitrate.

Keywords: Selectivity, Anion exchange, Resin matrix, Resin fixed ion.

INTRODUCTION

In separation of anions from the water and wastewater, selectivity plays important role as it reflects the preference of resin for particular ion in presence of other ions. Important factors governing anion selectivity in systems with monovalent and divalent ions include the spacing of the active sites, type of resin matrix, hydrophobic or hydrophilic nature of the resin matrix [1-3] and percentage of divinyl benzene [4]. The anion exchange selectivity data available for resins with polyacrylic matrix is inadequate, whereas anion exchangers with polystyrene matrix having cross linkages of divinyl benzene are used for exchange study of perchlorate and nitrate against chloride in aqueous and mixed media by various researchers [5,6]. Perchlorate and nitrate ions are hazardous to human health if their concentration in water is more than the permissible limit [7]. Hence, the present research deals with anion exchange selectivity of perchlorate and nitrate against chloride on weak base anion exchangers of different resin matrix at various temperatures in aqueous and mixed media. Anion exchangers used for the study are weak base Tulsion A-10X (MP), Amberlyst A-21 (MP) and strong base Tulsion A- 23 (Gel).

EXPERIMENTAL

Anion exchange resins Amberlyst A-21 (MP) from Himedia Laboratories Pvt. Ltd., Mumbai, India and Tulsion A-10X (MP) and Tulsion A-23 (Gel) resin samples received from Thermax Pvt., Ltd., Pune, India were used for the present work. Table-1 summarizes resin type, matrix structure and capacities of the resins used. All the reagents used were of analytical grade. The 0.05 M solutions of HCl, $HClO_4$, KNO_3 and KCl were prepared in water and water organic solvent mixed media.

Selectivity studies were carried out by taking 250 mg of air dried resin into 100 cm^3 stoppered volumetric flasks. 0.05 M electrolyte solutions of exchanging counter ions were added to the flask in different proportions to give a total volume of 30 cm^3 and total ionic strength of 0.05 M. The flasks were tightly closed and kept to attain equilibrium in reciprocate type Toshiba make mechanical shaker. After equilibration a known aliquot (10 cm^3) from external solution phase was pipetted out and estimated for Cl^- ions by Mohr's method using standard 0.05 M silver nitrate solution and potassium chromate as an indicator.

The selectivity coefficients $K_{c\,Cl^-}^{ClO_4^-}$ and $K_{c\,Cl^-}^{NO_3^-}$ were evaluated using the following equation.

$$RCl + B^- \rightleftharpoons RB + Cl^-$$

where $B^- = ClO_4^-, NO_3^-$

†Paper Presented at Recent Innovations in Process Engineering and Sustainability (RIPES-2016) held at Dr. M.S, Sheshgiri College of Engineering and Technology, Belgaum, India

TABLE-1
CHARACTERISTICS OF RESINS

Resin	Amberlyst A-21 (MP)	Tulsion A-10X (MP)	Tulsion A-23 (Gel)
Type	Weak base	Weak base	Strong base
Matrix structure	Styrene divinylbenzene (Macro porous)	Cross linked polyacrylic (Macro porous)	Styrene divinylbenzene (Gel)
Functional group	Tertiary ammonium	Polyamine	Quaternary ammonium
Ionic form	Base	Base	Base
Screen size (US mesh)	22-30	16-50	16-50
Total capacity (m.eq./250 mg)	0.720	0.900	0.830
Moisture content (%)	56-62	52±3	53

$$K_{c\,Cl^-}^{B^-} = \frac{\bar{N}_{RB}[Cl^-]}{\bar{N}_{RCl}[B^-]}$$

where $\bar{N}_{RB}$ and $\bar{N}_{Cl}$ are equivalent fractions of B^- and Cl^- in the resin phase.

Activity coefficients are not taken into account since the ionic strength of the electrolyte solution is 0.05 M. $\log K_{c\,Cl^-}^{B^-}$ values obtained were plotted against $\bar{N}_{RB}$ values. The least square values of $\log K_{c\,Cl^-}^{B^-}$ were evaluated using least square curve fitting for polynomial of degree 2. Averaged and corrected selectivity coefficient $\log K_{a\,Cl^-}^{''\,B^-}$ values obtained using method suggested by Ghate *et al.* [8] and Gupta [9] are represented in Tables 2 and 3. Resins of different types were used to investigate effect of temperature and solvent on selectivity.

TABLE-2
AVERAGE AND CORRECTED SELECTIVITY COEFFICIENT IN AQUEOUS MEDIUM

Anion exchanger	System	$\log K_{a\,Cl^-}^{''\,B^-}$ 303 K	313 K	323 K
Tulsion A-10X (MP)	ClO_4^-/Cl^-	-0.0474	-0.1385	-0.3539
	NO_3^-/Cl^-	0.3654	0.5219	0.5809
Amberlyst A-21 (MP)	ClO_4^-/Cl^-	1.5135	1.3689	1.3066
	NO_3^-/Cl^-	0.753	0.8107	0.8399
Tulsion A-23 (Gel)	ClO_4^-/Cl^-	1.1232	1.1167	1.0360
	NO_3^-/Cl^-	0.5365	0.5340	0.4237

RESULTS AND DISCUSSION

Effect of resin type: The selectivity sequence on Tulsion A-10X in aqueous medium (MP) is found to be $NO_3^- > ClO_4^- > Cl^-$ while for Amberlyst A-21 (MP) and Tulsion A-23 (Gel) it is $ClO_4^- > NO_3^- > Cl^-$.

$ClO_4^- > NO_3^- > Cl^-$ is the order expected from their crystallographic radii and the data in literature and can be explained by the models proposed by Diamond & Whitney [10] and Reichenberg [11]. Tulsion A-10X (MP) an acrylic resin shows greater affinity towards nitrate over perchlorate. The lower selectivity of perchlorate ions on acrylic resin can be attributed to the low hydration energy of perchlorate and different hydrophobicity of the matrix. On the other hand polyacrylic matrix tends to undergo greater hydration and imbibe more water molecules on polymer surface. This thicker hydration water layer of polyacrylic resin constitutes a more profound, rigid barrier on resin's surface, abating the ion pairing between perchlorate and functional amine groups of resin [12].

In contrast, for Amberlyst A-21 (MP) and Tulsion A-23 (Gel) polystyrene based resins having more hydrophobic matrix reduces the hydration barrier, which results in an enhanced ion pairing interactions between perchlorate and functional amine groups of resins. Hence perchlorate ion is more preferred on polystyrene based resin matrix than acrylic based resin matrix.

Effect of temperature: The effect of temperature on selectivity behaviour on binary systems ClO_4^-/Cl^- and NO_3^-/Cl^- in aqueous medium on weak base resins Tulsion A-10X (MP), Amberlyst A-21 (MP) and in aqueous and mixed media on strong base Tulsion A-23 (Gel) was studied at 303, 313 and 323 K. It is observed that the average and corrected selectivity coefficient values in aqueous medium for ClO_4^-/Cl^- system decrease with increase in temperature on all the three resins as represented in Fig. 1 and Table-2. This trend indicates the ion exchange reaction is exothermic [13]. The average and corrected selectivity coefficient values in aqueous medium for NO_3^-/Cl^- system increases with increase in temperature on

TABLE-3
AVERAGE AND CORRECTED SELECTIVITY COEFFICIENT IN 2-ISOPROPOXY ETHANOL AND 2-BUTOXY ETHANOL AT 303 ± 1 K, 313 ± 1 K AND 323 ± 1 K

Exchanging anion (B^-)	Exchanger	Temp. (K)	$\log K_{a\,Cl^-}^{''\,B^-}$ (at % w/w of) 2-Propoxyethanol 40	2-Propoxyethanol 80	2-Butoxyethanol 40	2-Butoxyethanol 80
ClO_4^-	Tulsion A-23 (Gel)	303	0.9490	0.5163	0.9407	0.7437
		313	0.9453	0.5037	0.9438	0.5815
		323	0.9208	0.5190	1.1137	0.6120
NO_3^-	Tulsion A-23 (Gel)	303	0.2530	-0.3170	0.3509	-0.1791
		313	0.2528	-0.2025	0.1069	-0.4343
		323	0.1867	-0.0655	0.1185	-0.3954

Tulsion A-10X (MP) and Amberlyst A-21 (MP), whereas it decreases with increase in temperature on Tulsion A-23 (Gel) as represented in Fig. 2 and Table-2. This trend indicates the ion exchange reaction is endothermic [14] on Tulsion A-10X (MP) and Amberlyst A-21 (MP) and exothermic on Tulsion A-23 (Gel). The free energy for exchange of NO_3^- on weak base resins decrease with increase in temperature, whereas it increases on strong base resin. This indicates that the exchange of NO_3^- is facilitated at high temperature on weak base resins but not preferred on strong base resin. The free energy data for exchange of ClO_4^- on both weak base resins show increase in free energy with increase in temperature, where as it decreases for strong base resin as represented in Table-4. The observed trend for the resins is due to change in resin fixed ion.

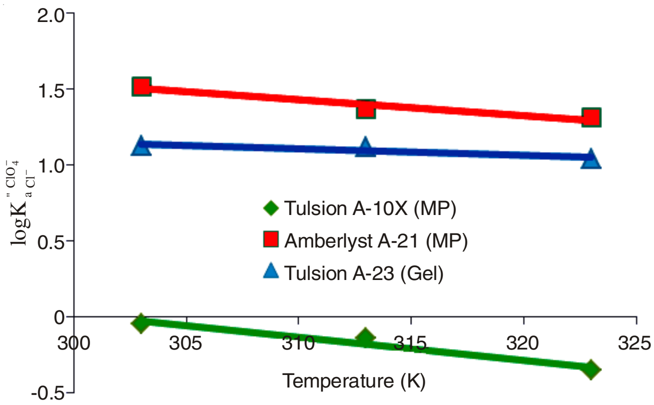

Fig. 1. $\log K''^{ClO_4^-}_{a\,Cl^-}$ *vs.* temperature for perchlorate exchange

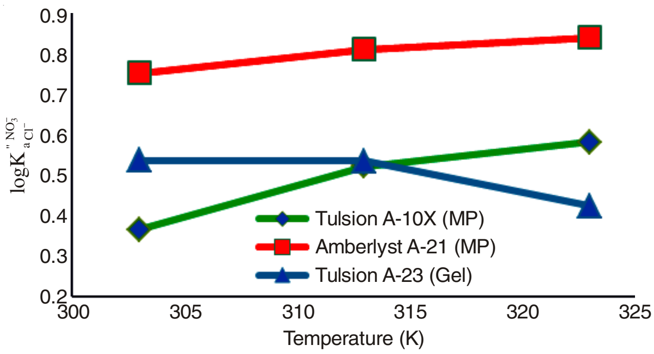

Fig. 2. $\log K''^{NO_3^-}_{a\,Cl^-}$ *vs.* temperature for nitrate exchange

Other thermodynamic parameters namely, change in enthalpy (ΔH) and entropy (ΔS) have also been determined. ΔH values are positive for NO_3^- exchange on both weak base resins whereas negative for strong base resin. The opposite trend is observed for ClO_4^- exchange. The positive values of ΔH show endothermic behaviour of exchange in aqueous medium. The endothermic nature of exchange also supports increase in K values with rise in temperature. The negative values of ΔH show exothermic behaviour of exchange in aqueous medium and as the temperature increases the K values decrease. The variation of ΔS along with ΔH points out changes in enthalpy that brings out randomness in the system. The randomness results due to increase in temperature.

TABLE-4
THERMODYNAMIC PARAMETERS IN AQUEOUS MEDIUM

System	Ion exchanger	ΔH°	ΔS°	Temp. (K)	ΔG°
ClO_4^--Cl	Tulsion A-23 (Gel)	-1.84	3.34	303	-2.86
				313	-2.93
				323	-3.00
	Tulsion A-10X (MP)	-21.85	-68.95	303	-0.96
				313	-0.26
				323	0.43
	Amberlyst A-21 (MP)	-15.91	-23.82	303	-8.69
				313	-8.45
				323	-8.21
NO_3^--Cl	Tulsion A-23 (Gel)	-2.39	-3.26	303	-1.40
				313	-1.33
				323	-1.27
	Tulsion A-10X (MP)	17.38	64.28	303	-2.09
				313	-2.74
				323	-3.38
	Amberlyst A-21 (MP)	4.11	27.83	303	-4.33
				313	-4.61
				323	-4.88

Effect of solvents: The effect of 2-isopropoxy ethanol and 2-butoxy ethanol on selectivity was studied on Tulsion A-23 (Gel) at three different temperatures. It is observed that the selectivity decreases with increase in the solvent content as shown in the Figs. 3 & 4 and Table-2.

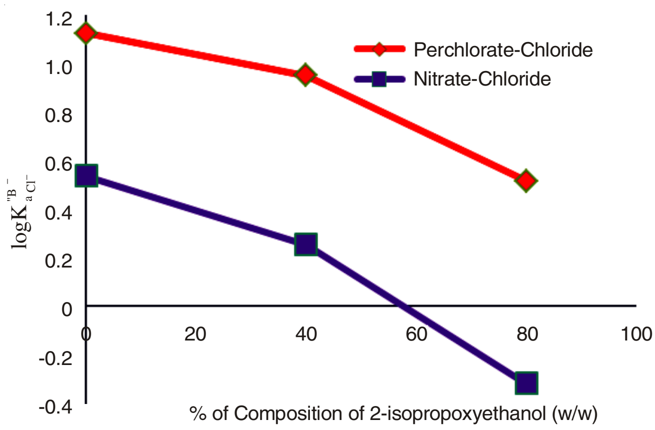

Fig. 3. $\log K''^{B^-}_{a\,Cl^-}$ *vs.* % composition of 2-isopropoxyethanol

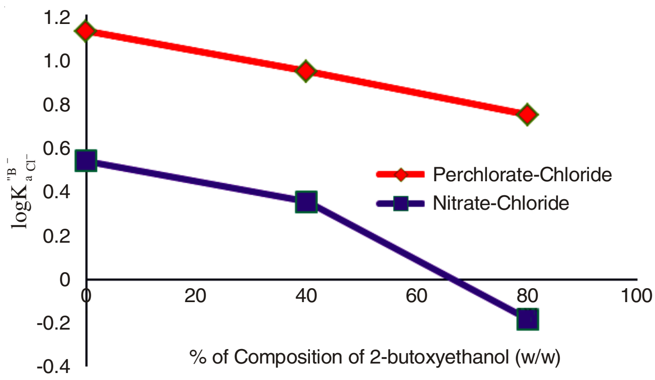

Fig. 4. $\log K''^{B^-}_{a\,Cl^-}$ *vs.* % composition of 2-butoxyethanol

At higher solvent composition the structure of the water is destroyed to a larger extent in the external solution phase than in the resin phase. Consequently the difference in the water structure in the two phases decreases with increased solvent content and hence the selectivity of the preferred anion will decrease with increase in organic solvent content.

There is decrease in the selectivity of perchlorate and nitrate ions in mixed media on Tulsion A-23 (Gel) with increase in temperature.

Conclusion

The results of exchange studies of perchlorate and nitrate against chloride on all the three resins indicate that weak base anion exchanger Amberlyst A-21 (MP) having polystyrene matrix is the most suitable for the separation of perchlorate and nitrate in aqueous medium at three different temperatures and perchlorate is least preferred on Tulsion A-10X (MP) with polyacrylic matrix. The selectivity decreases with increase in temperature for perchlorate exchange on all the resins while for nitrate it increases on weak base resins namely Tulsion A-10X (MP) and Amberlyst A-21 (MP). The presence of organic solvent in water also influences the selectivity. The selectivity for both the anions decreases with increase in organic solvent content.

ACKNOWLEDGEMENTS

The authors acknowledge their sincere thanks to Thermax Pvt. Ltd. Pune, India for providing different resin samples for this research work.

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