

Separation of anions from aqueous and mixed aqueous solvents using strong base and weak base anion exchangers

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ABSTRACT

Batch-wise sorption tests were carried out to evaluate the ability of strongly basic and weakly basic anion exchangers in chloride form to separate perchlorate, thiocyanate, iodide and nitrate anions from water/2-isopropoxy ethanol mixed media. The initial large difference observed in the selectivity magnitudes of ClO_4^- , CNS^- , I^- and NO_3^- decreased with increasing concentration of 2-isopropoxy ethanol. The higher selectivity of these anions on macroporous resins was attributed to higher degree of cross linkage. The addition of 2-isopropoxy ethanol changes the magnitude of solvation free energy of ions by replacing some of the water molecules in the coordination sphere. The important change observed in selectivity was due to significant reduction in dielectric constant of the medium from that of pure water to 80% 2-isopropoxy ethanol composition.

Keywords: Ion exchange; separation; mixed media; equilibrium; solvation

INTRODUCTION

Ion exchange resins comprise one of the most important scientific developments of the 20th century. Their applicability to water softening, environmental remediation, waste water treatment, chromatography, bimolecular separations and catalysis was recognized in numerous publications. Increasing levels of perchlorate, thiocyanate, iodide and nitrate in water and wastewater pose serious threats to water quality. 2-Isopropoxy ethanol is an organic compound used mainly as solvent and belongs to a class of solvents known as glycol ethers which have the ability to dissolve a variety of chemical compounds and are commonly used in paints, varnishes etc., which makes the possible entry into water and wastewater. In literature the selectivity data of anions in variety of mixed media is available viz., the substituted alcohols like, methoxy ethanol, ethoxy ethanol, butoxy ethanol etc. As 2-isopropoxy ethanol is miscible in water and behaves more aprotic solvent than 2-methoxy ethanol¹, is chosen for the present

study and the selectivity is proved to be governed by the protic or aprotic nature of the solvent. It is observed that the selectivity order on all strong base and weak base anion exchangers in aqueous medium was found to be $\text{ClO}_4^- > \text{CNS}^- > \text{I}^- > \text{NO}_3^- > \text{Cl}^-$. This was the order expected from their crystallographic radii and data in literature²⁻³. It is also in good agreement with reported models⁴⁻⁵ as well as previous investigators.⁶⁻⁷

Present paper deals with the separation of perchlorate, thiocyanate, iodide and nitrate from aqueous and mixed aqueous media using strong base and weak base anion exchangers in chloride form.

EXPERIMENTAL

Materials

Anion exchange resins Dowex 1X8 & Dowex 1X4 obtained from Dow Chemical Co., Amberlyst A-21 (MP) from Rohm and Hass Co., Philadelphia, USA and Tulsion A-27 (MP) &

Tulsion A-2X (Gel) gifted from Thermax Pvt., Ltd., Pune, India were used in present work.

The chemicals used were of all analytical grade reagents. The solvent 2-isopropoxy ethanol was obtained from E-Merck, Germany. The 0.05M solutions of HCl, HClO₄, HNO₃, KCl, KI and KCNS were prepared in water and water/2-isopropoxy ethanol mixed media.

Methods

Equilibrium studies were carried out by batch technique using different proportions of 0.05M solutions for ClO₄⁻-Cl⁻, CNS⁻-Cl⁻, I⁻-Cl⁻ and NO₃⁻-Cl⁻ systems with a fixed mass of dry resin beads into 100 cm³ glass stoppered Erlenmeyer flasks for a period of 6 hours in a reciprocate type of water bath incubator shaker. Exchange studies were carried out in 20, 40, 60 and 80 % of water/2-isopropoxy ethanol mixed media. After equilibration, the external solutions were estimated for Cl⁻ ions by suitable volumetric methods. In case of ClO₄⁻-Cl⁻ and NO₃⁻-Cl⁻ systems, Cl⁻ content of aliquots were determined by volhard's method and in case of CNS⁻-Cl⁻, and I⁻-Cl⁻ systems, CNS⁻ and I⁻ were determined by titration with standard potassium iodate solution.

Averaged and corrected selectivity coefficients $K_{a \text{ Cl}^-}^{B^-}$ for anions on different resins in water and water/2-isopropoxy ethanol mixed media were calculated using the method of Ghate et. al.⁸ and Gupta A. R.⁹

The present study has been carried out to show how the increasing percentage of organic solvent influences the separation of anions using different anion exchange resins. These results have been obtained with regard to separation of anions from water and wastewater containing organic solvent.

In mixed-media, as 2-isopropoxy ethanol replaces water, the external phase water mole fraction decreases more rapidly than that of the resin phase and anions uptake by the relatively water-rich resin phase increases. Similarly, a small, basic anion finds increasingly poorer solvation in the external phase as the organic (2-isopropoxy ethanol) mole fraction increases, so its binding to the external solution decreases and its distribution into the resin increases.¹⁰⁻¹¹ Thus, in mixed media the structure of water or structure of solvation shell in the external phase is destroyed to a greater extent, because solvent occupies some space and

molecules form much less three dimensional hydrogen bonding. At the same time, structure of water in the resin phase is affected to a lesser extent. Consequently the difference in water in two phases decreases with increase in 2-isopropoxy ethanol content. Hence the selectivity of the preferred anion in aqueous medium should decrease with increase in 2-isopropoxy ethanol content.

This can be seen from figures 1, 2, 3, 4 and 5 that there is decrease in selectivity of all anions on all the resins with increase in 2-isopropoxy ethanol content. The decrease in selectivity on strong base anion exchangers is rather steep in the case of ClO₄⁻, CNS⁻ compared to that of I⁻ and NO₃⁻. There is a crossover of selectivity between CNS⁻ and I⁻ on Dowex 1X8 and Dowex 1X4 at 5% and on Tulsion A-27 (MP) at about 15% solvent composition.

Thus, the selectivity sequence in aqueous medium changes to ClO₄⁻ > I⁻ > CNS⁻ > NO₃⁻ > Cl⁻ on all the resins in mixed media beyond 15% solvent composition. At solvent compositions beyond 65% because of cross overs and selectivity reversal, the selectivity sequence observed is I⁻ > ClO₄⁻ > CNS⁻ > Cl⁻ > NO₃⁻. However on Dowex 1X4 this selectivity sequence becomes ClO₄⁻ > I⁻ > CNS⁻ > Cl⁻ > NO₃⁻ due to second cross over taking place between I⁻ and ClO₄⁻ at about 70% solvent composition.

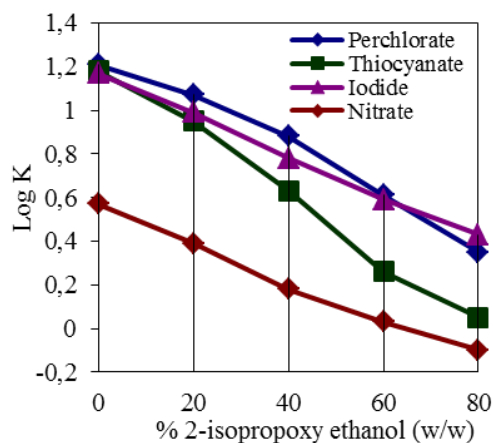


Figure 1 logK vs. 2-isopropoxy ethanol on Dowex 1X8

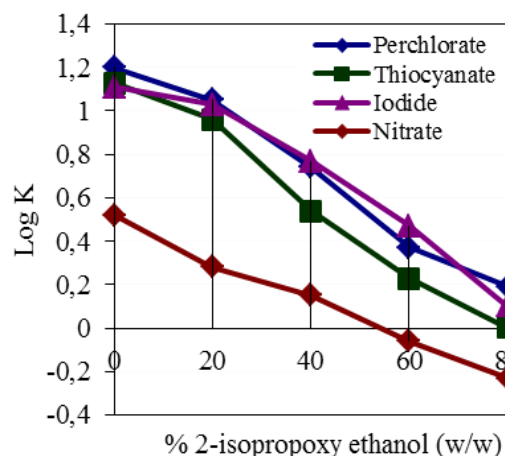


Figure 2 $\log K$ vs. 2-isopropoxy ethanol on Dowex 1X4

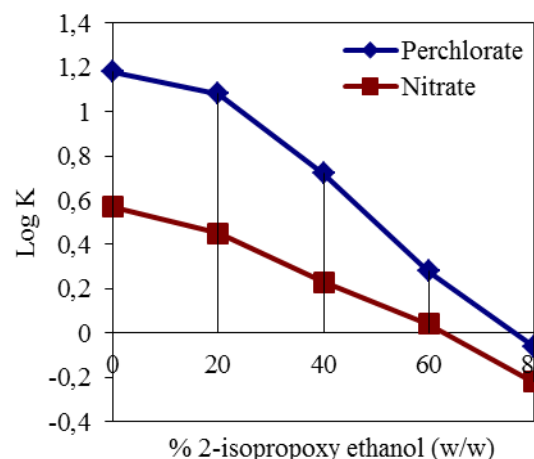


Figure 5 $\log K$ vs. 2-isopropoxy ethanol on Amberlyst A-21 (MP)

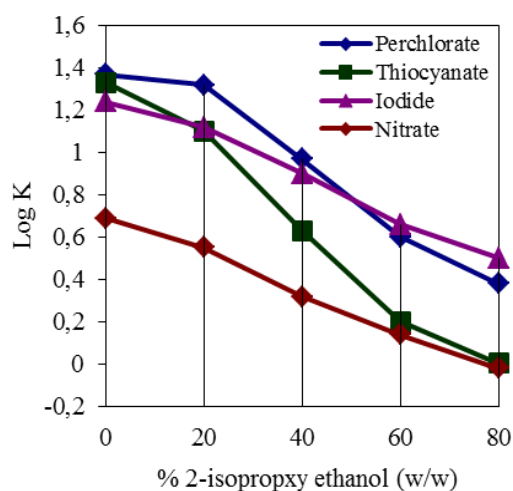


Figure 3 $\log K$ vs. 2-isopropoxy ethanol on Tulsion A-27 (MP)

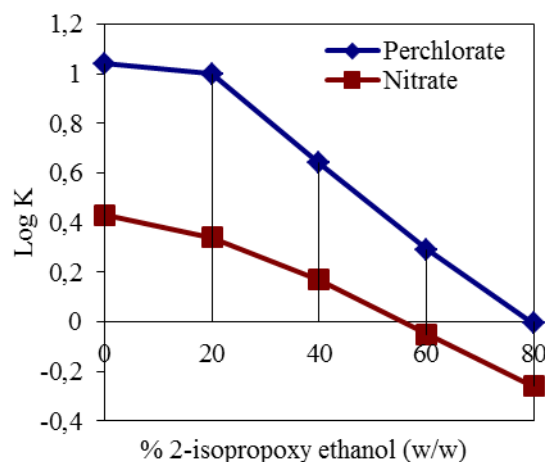


Figure 4 $\log K$ vs. 2-isopropoxy ethanol on Tulsion A-2X (Gel).

Similarly in case of weak base anion exchangers the selectivity reversal is observed around 65% solvent composition for NO_3^- on Tulsion A-2X, where Cl^- is preferred to NO_3^- . The initial large difference in the selectivity magnitudes of ClO_4^- and NO_3^- goes on decreasing as solvent composition increases, because of greater ion solvent interaction for ClO_4^- in mixed solvent medium. Selectivity reversal is also observed on Amberlyst A-21 for ClO_4^- and NO_3^- around 65 and 75% solvent compositions respectively.

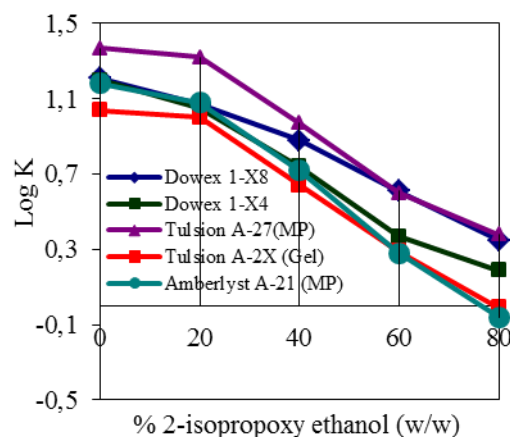


Figure 6 $\log K_a^{\text{ClO}_4^-/\text{Cl}^-}$ vs. 2-isopropoxy ethanol on all resins.

Dielectric constant is a macroscopic property of liquids. The dielectric constant of pure water is 78.54 ($\epsilon = 78.54$) at 298 K and that of 2-isopropoxy ethanol is 10.5 ($\epsilon = 10.5$). Thus, there will be continuous decrease in dielectric constant from 78.54 to 10.5 upon addition of 2-

isopropoxy ethanol to water. Though the dielectric constant of the medium is not the dominating factor in the determination of selectivity, but the experimental selectivity data support in this context.

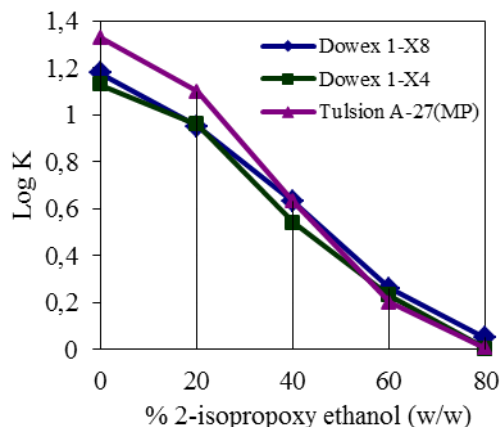


Figure 7 $\log K_{a, Cl^-}^{CNS^-}$ vs. 2-isopropoxy ethanol on Dowex 1X8, Dowex 1X4 and Tulsion A-27(MP)

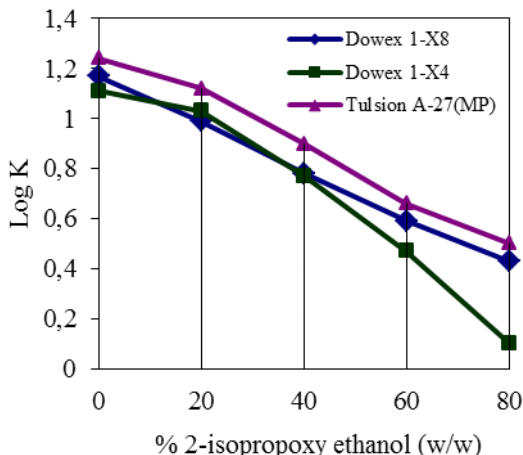


Figure 8 $\log K_{a, Cl^-}^{I^-}$ vs. 2-isopropoxy ethanol on Dowex 1X8, Dowex 1X4 and Tulsion A-27 (MP)

Effect of variation of cross linking (% divinyl benzene) of the exchanger on selectivity

Exchange studies were carried out on differently cross linked resins like Dowex 1X8 and Dowex 1X4 and the results were compared with those on Tulsion A-27 (MP), Tulsion A-2X (Gel) and Amberlyst A21 (MP). The number of water molecules available per exchange site in an exchanger generally decreases with increase in cross linkage, because there is decrease in swelling of resin bed with increase in the divinyl benzene (DVB) content. In other words electrolyte concentration in the resin phase increases with cross linkage and therefore the

selectivity of preferred anion should increase with increase in cross linkage irrespective of the solvent composition in the external phase. The variation of $\log K_{a, Cl^-}^{B^-}$ as a function of 2-isopropoxy ethanol content of the medium for each cross linkage is depicted in figures 6, 7, 8 and 9. Similar observation of the effect of cross linking with cations and anions on corresponding strong exchangers were reported by Myers et.al.¹²

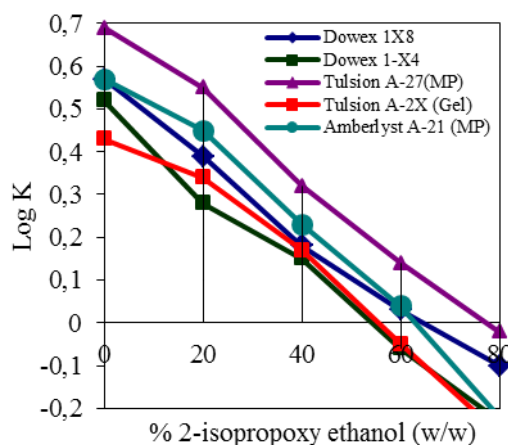


Figure 9 $\log K_{a, Cl^-}^{NO_3^-}$ vs. 2-isopropoxy ethanol on all resins

Selectivity order was also confirmed by free energy data. Qualitatively the same selectivity order was obtained by free energy data. The free energy data for exchange of ClO_4^- , CNS^- , I^- and NO_3^- in water/2-isopropoxy ethanol shows (Table 1) increase in free energy change with increase in percentage of 2-isopropoxy ethanol in solution. This implies that exchange is facilitated in aqueous medium as compared to solvent medium. The free energy change has negative values and become less negative/positive values with increase in 2-isopropoxy ethanol percentage. The macro porous resin contains pores or channels of several hundred nanometers in diameter even in dry state. Increase in the usable capacity of the resin is due to the penetration of electrolyte in the grains by Donnan equilibrium. It follows therefore that a great proportion of functional sites are found to be direct contact with solution and that distribution is partially replaced by the easier migration in the solution contained in the pores of the grains. Thus, higher selectivity of ClO_4^- , CNS^- , I^- and NO_3^- on Tulsion A-27 and Amberlyst A-21 is attributed to macro porous nature of the resin.

CONCLUSIONS

In general, the selectivity of all anions on all resins studied, decreases with increase in 2-isopropoxy ethanol content. It was observed that the selectivity order of anions studied was influenced by crystallographic radii of anions, water structure in mixed media and cross linking of resins. In case of Tulsion A-27 and Amberlyst A-21 the selectivity values were high due to higher degree of cross linkage in macroporous resins. Similarly, the selectivity values were high in case of Dowex 1X8 than in Dowex 1X4 due to higher cross linkage. However, when organic

content was increased in mixed solvent, hydrated ions were squeezed out of the solution phase into the resin phase which was comparatively having more structured water. The free energy data for exchange of anions in mixed media has shown that the selectivity was more in aqueous medium than compared to mixed solvent medium. Thus, the study has shown that these strong base and weak base anion exchangers in chloride form can be employed for the separation ClO_4^- , CNS^- , I^- and NO_3^- from aqueous and mixed aqueous solvents.

Table 1. Thermodynamic free energy data for exchange of anions against chloride of the resin phase in water/2-isopropoxy ethanol mixed media at $303 \pm 1\text{K}$ with standard deviation

Resin	Exchanging anion	ΔG (kcal mol ⁻¹)				
		00	20	40	60	80
Dowex 1X8	ClO_4^-	-1.67±0.03	-1.48±0.09	-1.22±0.07	-0.84±0.02	-0.48±0.05
	CNS^-	-1.63±0.09	-1.31±0.10	-0.87±0.05	-0.36±0.04	-0.07±0.03
	I^-	-1.62±0.11	-1.37±0.12	-1.08±0.08	-0.81±0.07	-0.59±0.05
	NO_3^-	-0.79±0.08	-0.54±0.07	-0.25±0.01	-0.04±0.03	+0.14±0.06
Dowex 1X4	ClO_4^-	-1.66±0.05	-1.45±0.08	-1.02±0.10	-0.51±0.07	-0.26±0.05
	CNS^-	-1.56±0.07	-1.33±0.08	-0.75±0.10	-0.32±0.05	-0.003±0.0
	I^-	-1.53±0.07	-1.42±0.11	-1.06±0.09	-0.65±0.06	-0.14±0.02
	NO_3^-	-0.72±0.06	-0.39±0.06	-0.21±0.04	+0.08±0.02	+0.32±0.05
Tulsion A-27 (MP)	ClO_4^-	-1.89±0.09	-1.82±0.08	-1.34±0.11	-0.83±0.08	-0.52±0.07
	CNS^-	-1.84±0.07	-1.52±0.13	-0.87±0.11	-0.28±0.02	-0.01±0.00
	I^-	-1.71±0.10	-1.55±0.04	-1.24±0.08	-0.91±0.08	-0.69±0.08
	NO_3^-	-0.95±0.04	-0.76±0.11	-0.44±0.05	-0.19±0.03	+0.03±0.00
Tulsion A-2X (Gel)	ClO_4^-	-1.44±0.10	-1.38±0.10	-0.88±0.05	-0.40±0.05	+0.01±0.00
	NO_3^-	-0.59±0.04	-0.47±0.05	-0.23±0.05	+0.07±0.02	+0.36±0.05
Amberlyst	ClO_4^-	-1.63±0.05	-1.49±0.12	-0.99±0.09	-0.39±0.04	+0.08±0.02
A-21 (MP)	NO_3^-	-0.79±0.11	-0.62±0.06	-0.32±0.03	-0.06±0.02	+0.30±0.07

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