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EFFECT OF SOLVENTS ON ION EXCHANGE SELECTIVITY OF MONOVALENT ANIONS ON TULSION A-27 (MP)

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ABSTRACT

The exchange of monovalent anions perchlorate and nitrate against Cl^- were investigated as a function of organic solvent compositions from aqueous to 80% mixed solvent media at 300 ± 1 K on strong base anion exchanger Tulsion A-27 (MP). Selectivity coefficients were determined over the wide range of resin mole compositions ($N_{RB} = 0$ to 1) for the resin to understand the effect of organic solvents. The selectivity values of these anions in water-2-methoxy ethanol on Tulsion A-27 (MP) are higher than those compared with water-2-isopropoxy ethanol, water-2-butoxy ethanol and water-2-ethoxy ethanol and there is drastic change in the selectivity coefficient values for these anions in case of water-2-ethoxy ethanol at higher solvent compositions. Thermodynamics of ion exchange has shown that anion exchange is more in aqueous medium than in mixed solvent medium.

Key words: Selectivity, Anion exchange, Mixed media, Dielectric constant, Ion-pair.

INTRODUCTION

The selectivity is an important property of an ion exchanger to exhibit preferentiality for certain ions in a solution containing several ions. Systematic studies of ion exchange equilibria among simple inorganic anions in various water miscible organic solvents on anion exchangers were investigated with a view to learn the influence of water miscible organic solvents on exchange selectivity behavior and their use in improving the resolution and speed of separation[1-5]. Many organic solvents with varied solvent properties such as protic and aprotic in nature, dielectric constant, dipole moment, etc. have been used to study the behavior of ion exchange selectivity in mixed solvent systems and the study has shown dielectric constant may not have the significant contribution to selectivity as was envisaged earlier. This work focuses on effect of solvents on selectivity of ClO_4^- and NO_3^- against Cl^- in water and mixed media. Substituted alcohols, 2-methoxy ethanol and 2-ethoxy ethanol,

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have been used for the exchange study of anions such as perchlorate and nitrate against chloride on strong base resin Tulsion A-27 (MP) and the selectivity values are compared with water-2-isopropoxy ethanol and water-2-butoxy ethanol.

EXPERIMENTAL

Ion exchange resins and solvents

The strong base anion exchanger Tulsion A-27 (MP), obtained from Thermax Pvt. Ltd., Pune was reconditioned by treatment with 1 M sodium hydroxide and 1 M hydrochloric acid alternatively. Finally, the resin was converted into chloride form by passing an excess amount of 1 M HCl solution. Resin was thoroughly washed with double distilled water till the washings were free from chloride. The air dried resin was used for experimental studies.

All reagents used were of AR grade. Substituted alcohols 2-methoxy ethanol and 2-ethoxy ethanol were used of Acros organics, USA. 0.05 M solutions of potassium chloride, potassium nitrate, hydrochloric acid and perchloric acid were prepared in water and water-mixed media and standardized before use.

Determination of selectivity coefficient

Equilibrium studies were carried out by taking 250 mg of air dried resin beads into 100 cm^3 stoppered 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. For the exchange study in mixed medium, electrolyte solutions prepared in 20, 40, 60 and 80 % (w/w) of 2-methoxy ethanol and 2-ethoxy ethanol were taken. The flasks were tightly closed and kept for shaking for 8 hours with reciprocate type of water bath mechanical shaker. After equilibration, a known aliquot from external solution phase was used for the estimation of Cl^- ions by Mohr's method. The selectivity coefficients $K_C{}^{ClO_4^-}_{Cl^-}$ and $K_C{}^{NO_3^-}_{Cl^-}$ were evaluated using the following equation.

$$RCl + B^- \rightleftharpoons RB + Cl^- \qquad \ldots(1)$$

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

$$K_C{}^{B^-}_{Cl^-} = \frac{\overline{N}_{RB}[Cl^-]}{\overline{N}_{RCl}[B^-]}$$, where $\overline{N}_{RB}$ and $\overline{N}_{RCl}$ 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 $\overline{N}_{RB}$ 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 $K''^{B^-}_{a\,Cl^-}$ in water and water-mixed media were calculated[6]. Table 1 summarizes data for averaged and corrected selectivity coefficients of anions on strong base resin Tulsion A-27 (MP) for water and water- mixed media.

Table 1: Averaged and corrected selectivity coefficients for anions on Tulsion-A 27 (MP) in 2-methoxy ethanol and 2-ethoxy ethanol mixed media at 303 ± 1 K

Solvent used	**Exchanging anion**	**Log $K''^{B^-}_{a\,Cl^-}$**				
		00%	**20%**	**40%**	**60%**	**80%**
2-Methoxy ethanol	**ClO_4^-**	1.52	1.42	1.08	0.95	0.48
	NO_3^-	0.63	0.61	0.50	0.21	-0.11
2-Ethoxy ethanol	**ClO_4^-**	1.52	0.99	0.38	0.26	0.21
	NO_3^-	0.63	0.52	0.31	-0.045	-0.35

RESULTS AND DISCUSSION

Selectivity behaviour in aqueous medium

The selectivity sequence in aqueous medium for the resin is $ClO_4^- > NO_3^- > Cl^-$. This is the order expected from their crystallographic radii and the data in literature[4,6]. A small ion with high charge density such as Cl^- has more negative free energy of hydration compared to a larger one like ClO_4^- with low charge density. Cl^- will therefore prefer the external aqueous phase to satisfy hydration better. The quaternary ammonium group in the resin phase is a larger hydrophobic ion with low charge density. It will create a cavity resulting in tightening of water structure, which in turn decreases the entropy of the system. A larger ion such as ClO_4^- with low charge density also tries to create a cavity and tighten up the water structure, which might further reduce the entropy of the system. But in order to avoid this further decrease in entropy, the two ions (R^+ and larger ClO_4^- anion) are forced to share a single cavity; thus, favoring the formation of an ion pair. This is known as water-structure-enforced ion pairing[7].

Selectivity behaviour in mixed medium

In mixed medium, the water structure 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 the water in the two phases decreases with increased solvent content. Hence, the selectivity of the preferred anion in aqueous medium should decrease with increase in organic solvent content.

It can be seen from Figs. 1 and 2 that there is decrease in selectivity of ClO_4^- and NO_3^- anions on the resin Tulsion A-27 (MP) with increase in organic solvent content. This decrease in selectivity is rather steep in case of ClO_4^- and NO_3^- in 2-ethoxy ethanol mixed media compared to that of 2-methoxy ethanol mixed media. There is a selectivity reversal between NO_3^- and Cl^- above 60% solvent composition on Tulsion A-27 (MP). This reversal in selectivity may be used to regenerate the resin in original Cl^- form. Due to the higher concentration of organic solvent in the external phase, the relative concentration of water in the resin phase will be higher than in the external solution phase resulting in predominance of water-structure-enforced ion pairing. As shown in Table 2, the free energy data for exchange of ClO_4^- and NO_3^- in mixed media increases with increase in percentage of solvent content indicating that exchange is facilitated in aqueous medium than in mixed solvent medium. The free energy change has negative values and become positive with increase in solvent percentage.

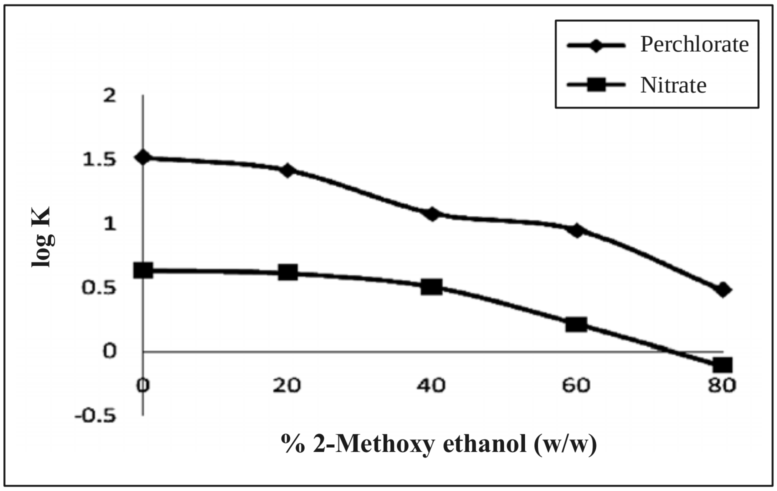

Fig. 1: $\log K''_{a}{}^{B^-}_{Cl^-}$ vs % 2-methoxy ethanol (w/w) on Tulsion A-27(MP)

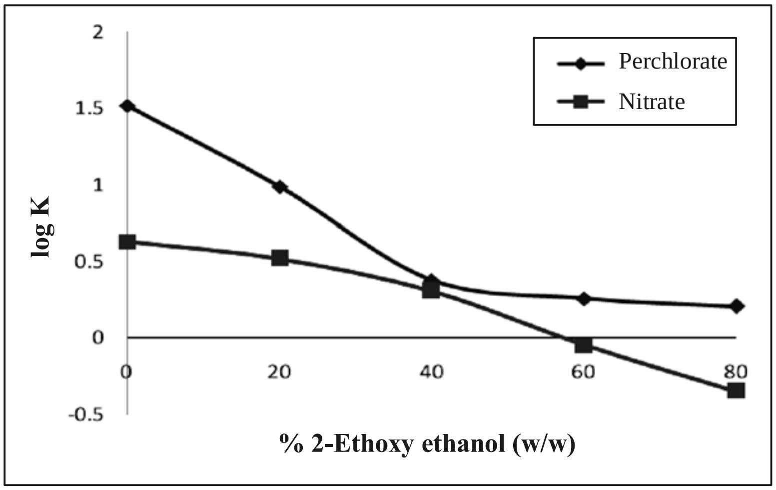

Fig. 2: log $K_a'' \frac{B^-}{Cl^-}$ vs % 2- Ethoxy ethanol (w/w) on Tulsion A-27(MP)

Table 2: Thermodynamic free energy data for exchange of anions against chloride of the resin phase in 2-methoxy ethanol and 2-ethoxy ethanol mixed media at 303 ± 1 K

Percentage of solvent (w/w)	ΔG (Kcal mol^{-1})			
	2-Methoxy ethanol		2-Ethoxy ethanol	
	ClO_4^- / Cl^-	NO_3^- / Cl^-	ClO_4^- / Cl^-	NO_3^- / Cl^-
00	-2.10	-0.87	-2.10	-0.87
20	-1.96	-0.84	-1.37	-0.72
40	-1.49	-0.69	-0.52	-0.43
60	-1.31	-0.29	-0.36	+0.06
80	-0.66	+0.15	-0.29	+0.48

Effect of dielectric constant of organic solvents on anion exchange selectivity

The results of exchange studies on Tulsion A-27 (MP) in mixed organic solvents, 2-methoxy ethanol and 2-ethoxy ethanol were compared with 2-isopropoxy ethanol[1] and 2-butoxy ethanol[8]. In ion exchange selectivity, the macroscopic dielectric constant value of the solvent medium affects the degree of ion-pair formation but the protic and aprotic nature of the solvent is more dominating than its dielectric constant. Further, 2-ethoxy ethanol is more aprotic than 2-methoxy ethanol and accordingly Figs. 3 and 4 show the selectivity magnitudes are generally lower in 2-ethoxy ethanol compared to those in 2-methoxy ethanol.

Thus, for the same reason, we may expect lower selectivity values in case of 2-isopropoxy ethanol and 2-butoxy ethanol.

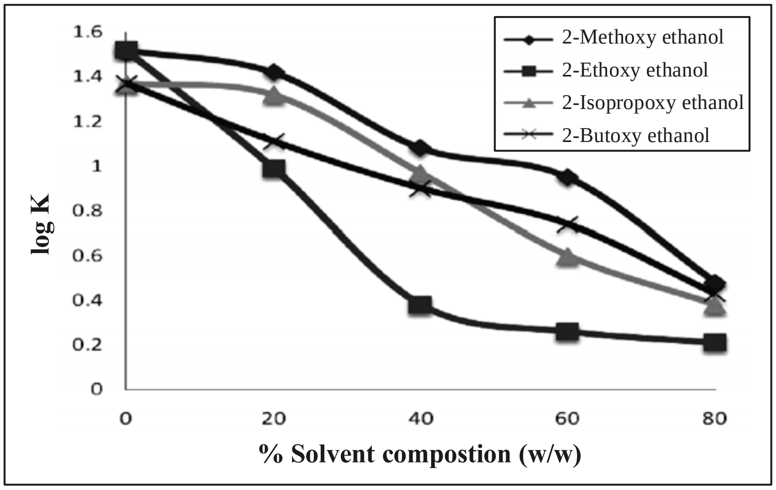

Fig. 3: log $K''_{a}{}^{ClO_4^-}_{Cl^-}$ vs % solvent composition (w/w) on Tulsion A-27(MP)

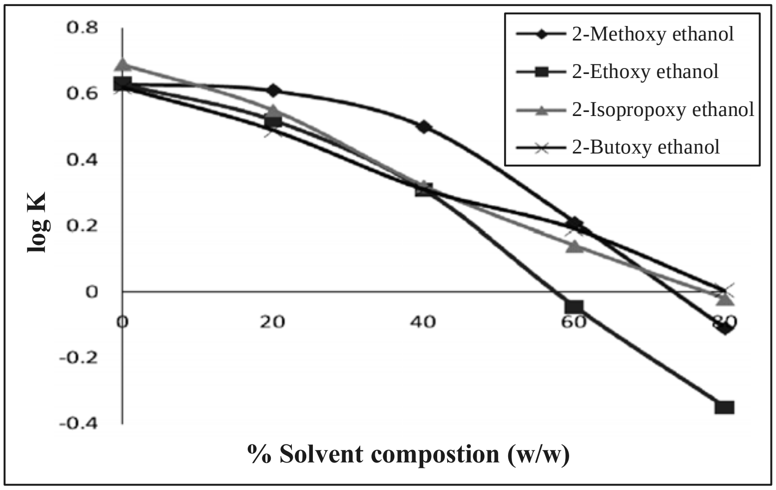

Fig. 4: log $K''_{a}{}^{NO_3^-}_{Cl^-}$ vs % solvent composition (w/w) on Tulsion A-27(MP)

CONCLUSION

In general, the selectivity of anions ClO_4^- and NO_3^- on resin Tulsion A-27 (MP) studied decreases with increase in organic solvent content. Effect of solvents on anion exchanger Tulsion A-27 (MP) is also observed as the selectivity decrease is steep in the case of ClO_4^- and NO_3^- in 2-ethoxy ethanol mixed media compared to other mixed media. Further, the dielectric constant of the solvent no doubt, affects the degree of ion-pair formation and hence influences the transport and thermodynamic properties of the electrolyte solutions. But, the protic and aprotic nature of the solvent is more dominating factor than its dielectric constant in governing ion exchange selectivity.

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