Separation of Trace Metal as Oxoanions from Contaminated Water

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Ion exchange technique has been employed to remove trace metals from contaminated water by batch process and the ability of strongly basic anion exchanger Amberlite IRA-400 in nitrate form has been evaluated to separate chromium, molybdenum and tungstan as oxoanions *viz* chromate, molybdate and tungstate. Conclusions have been drawn regarding the variation of selectivity coefficient with change in solvent composition of mixed solvents such as aqueous methanol, aqueous ethanol and aqueous isopropanol. Thermodynamics of ion exchange has also been studied. The data indicates that strongly basic anion exchanger Amberlite IRA-400 in nitrate form has got good potential for separation of these oxoanions and exchange of anions increased with increase in temperature and alcoholic content. Particle size and quantity of resin also have remarkable effect on exchange.

**Key Words: Ion exchange, Chromate, Molybdate, Tungstate.**

INTRODUCTION

In recent years the chemistry and biology of chromium, molybdenum and tungsten have been the subject of increasing attention due to their importance as essential and toxic elements. The major source of trace matters are waste water from electro-plating and metal finishing industries[1-3]. In biological system chromium(III) is non toxic and is an essential trace nutrient in human diet. On the other hand chromium(VI) is very toxic to man, animals and plants and classified by the US Environmental Protection Agency (EPA) as a group A human carcinogens. The molybdenum is an essential constituent of enzymes, which catalyzes redox reactions and help in nitrogen fixation[2-4] while at relatively high doses the molybdenum salts produce positive genotoxicity both in human cells and in mice. Tungsten plays an important role in some enzymes which convert CO_2 into formic acid, however when present in excess tungsten is found to be harmful for plants and animals. Equilibrium studies for anions in aqueous solvents are comparatively less[5-9] and oxoanions anions in partly aqueous solvents have not been studied so far. Ion exchange technique has been used in present work to study systematically the exchange of CrO_4^{2-}, MoO_4^{2-} and WO_4^{2-} ions in aqueous methanol, aqueous ethenol and aqueous isopropanol solvent against the NO_3^- form of strongly basic anion exchanger amberlite IRA-400 to achieve maximum separation of these oxoanions.

EXPERIMENTAL

The strongly basic anion exchange resin, amberlite IRA-400 (BDH, AR), is polytrimethl vinyl benzyl ammonium type of strongly basic anion exchanger. The resin available in the chloride form, was converted into nitrate form.

The ion exchange capacity of air dried resin (40-60 mesh) was found to be 3.5 meq/g. This resin separates oxoanions from aqueous waste by exchanging the nitrate ions of the resin with oxoanions as shown in reaction

$$2\,[A\text{-}NO_3^-] + [MO_4^{2-}] \rightarrow [A\text{-}MO_4^{2-}] + 2[NO_3^-]$$
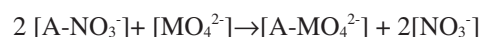
where, M = Cr, Mo and W

Selectivity studies were carried out by batch technique using 50 mL of oxoanion solution in mixed solvents containing alcohol percentage from 0-40 % and 1 g of anion exchange resin in glass stoppered Erlenmeyer flask. It was kept in a water bath shaker for 24 h to attain the equilibrium. After equilibration, aliquots were analyzed for oxoanions by spectrophotometeric method. Selectivity data was recorded with respect to change in solvent composition and temperature. The effect of solvent composition on thermodynamic parameters, *viz*. ΔF, ΔH and ΔS and rate of exchange of oxoanions has also been studied. The data has been reported in terms of selectivity coefficient given by the following expression:

Alcohol (%)	Methanol			Ethanol			Isopropanol		
	CrO_4^{2-}	MoO_4^{2-}	WO_4^{2-}	CrO_4^{2-}	MoO_4^{2-}	WO_4^{2-}	CrO_4^{2-}	MoO_4^{2-}	WO_4^{2-}
00	0.226	1.713	1.767	0.266	1.713	1.767	0.266	1.713	1.767
10	0.297	1.758	1.775	0.308	1.767	1.786	0.440	1.893	1.810
20	0.356	1.838	1.792	0.425	1.880	1.811	0.672	1.980	1.823
30	0.425	1.848	1.795	0.525	1.973	1.835	0.784	2.102	1.838
40	0.549	1.979	1.843	0.741	2.057	1.874	0.786	2.120	1.879

TABLE-1
EFFECT OF SOLVENT ON THE SELECTIVITY OF OXOANIONS AGAINST THE NITRATE IONS OF THE RESIN PHASE

$$K' = \frac{X_{B*R}}{(X_{AR})^*} \times \frac{(C_{AS})^*}{C_{B*S}}$$

where, X_{B*R} and X_{AR} are the equivalent fractions of exchanged ions and nitrate ions in the resin phase respectively and C_{AS} and C_{B*S} are the ionic concentration terms for the liberated and the exchanged counter ion in solution phase. As K' values were found to vary with X_{BR}, a method of graphical integration was applied to find out the corrected selectivity constant (K).

RESULTS AND DISCUSSION

The data obtained show how the increasing percentage of organic solvents influences separation of oxoanions and how this process is influenced by rise in temperature. The corrected selectivity coefficient for oxoanions (chromate, molybdate and tungstate) /nitrate ion exchange varies with solvent composition as shown in Table-1.

As it is clear from data that the exchange increases with increase in percentage of the organic solvent from 0-40 %. As the percentage of organic solvent increases in the outside solution, the water structure breaks down in this medium. However, this breakdown is less inside the resin phase as compared to the outside solution. The smaller ions, therefore. prefer the resin phase more than the solution phase.

Since the hydration of ion is inversely related with the ionic radii, the smallest ion has the strongest interaction with water and forms the largest hydrated ion. In aqueous solution, exchange of ion is usually more for the smaller hydrated ion. The oxoanion chromate (ionic radius 44 pm) forms the largest hydrated ion in comparison to molybdate (ionic radius 59 pm) and tungstate (ionic radius 60 pm). The observed sequence is same as expected from theoretical consideration in organic solvents.

Effect of temperature on selectivity of oxoanion/ nitrate exchange in aqueous methanolic solvent shows that with increase in temperature the extent of exchange also increases at fixed solvent composition. Thus rise in temperature is expected to increase the solvation of ionic species in solutions.

TABLE-2
EFFECT OF TEMPERATURE ON SELECTIVITY

	log K (CrO_4^{2-})			
Methanol (%)	30 ℃	35 ℃	40 ℃	45 ℃
00	0.138	0.266	0.295	0.297
10	0.191	0.297	0.425	0.525
20	0.255	0.356	0.440	0.659
30	0.425	0.425	0.549	0.739
40	0.514	0.549	0.739	1.119

The free energy data for exchange of oxoanion in aqueous methanol shows decrease in free energy change with increase in methanol percentage in solution. This implies that exchange is facilitated in alcoholic solution as compared to aqueous medium. The free energy change has negative values (Table-3) and negativity increases with increase in methanol percentage. The other thermodynamic parameters namely change in enthalpy and entropy has also been determine for the exchange process.

The positive value of ΔH shows endothermic behaviour of exchange. The endothermic nature of exchange also support increase in selectivity with rise in temperature.

Variation of ΔS alongwith ΔH points out changes in enthalpy that brings out randomness in the system. The methanol percentage may create a sort of disorder in the water structure so that entropy changes in aqueous methanol can be co-related to disorder. The above contention that increase in randomness results due to increase in temperature since, with rise in temperature the chemical processes in solution like association of ions etc., is not supported.

TABLE-3
EFFECT OF THERMODYNAMIC PARAMETERS ON EXCHANGE OF OXOANIONS AGAINST NITRATE IONS OF THE RESIN PHASE

Exchange	Methanol (%)	ΔF (kcal mol^{-1})		ΔH (kcal mol^{-1})	ΔS (cal mol^{-1})
MoO_4^{2-} /NO_3^-	00	-2.2076	-2.5182	7.202	31.0550
	10	-2.3519	-2.7017	8.2471	34.9800
	20	-2.5960	-2.8536	5.2079	25.7550
	30	-2.4803	-2.8818	9.6849	40.1490
	40	-2.6453	-3.1285	11.9950	48.3180

The kinetic study for exchange of oxoanions/nitrate ion shows that the exchange process is not time-consuming (Table-4). The slow rate of exchange may be due to exchange of these bigger anions against smaller nitrate ions. Moreover, it is observed that increase in alcohol percentage makes the exchange rate slow.

The resin particle size plays an important role in deciding the exchange of ions. In the present study, two particle sizes of the resin, 20-40 mesh and 40-60 mesh, have been used and selectivity data has been collected for chromate/nitrate exchange in mixed methanolic solvent. It is clear that smaller size particles show more exchange than the bigger size particles. As the exchange involves exposed surface area, for the given amount of ion exchanger, smaller the particle size more is the surface are available for exchange (Fig. 1).

<center>TABLE-4
KINETIC STUDY FOR EXCHANGE OF OXOANIONS
AGAINST THE NITRATE ION</center>

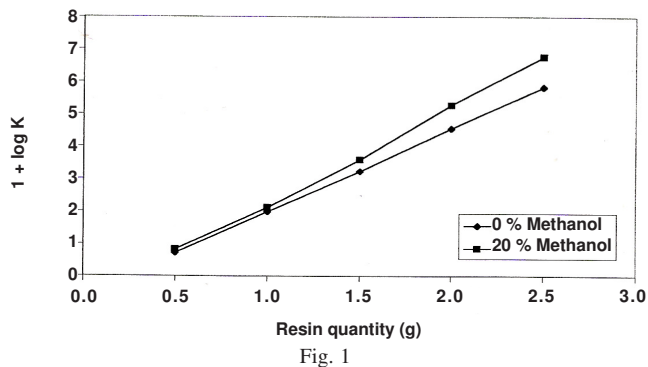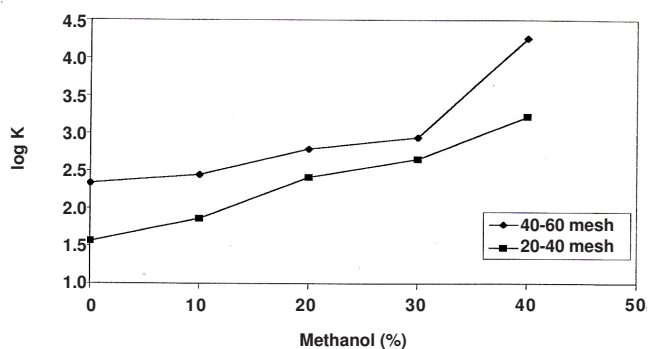| Exchange	Methanol %	Equilibrium time (min)	$t_{1/2}$ (min)
CrO_4^{2-}/NO_3^-	00	50	07
	20	60	12
	40	75	18
MoO_4^{2-}/NO_3^-	00	60	10
	20	92	16
	40	113	40
WO_4^{2-}/NO_3^-	00	74	13
	20	101	25
	40	116	42

Fig. 1

Conclusion

Ion exchange is dependent on the ionization of the electrolyte in solution, but the present studies show that factor other than simple ionization can be the deciding factor for any exchange to occur, hence no generalization can be made for studies in mixed solvents. The water structure involvement must be considered to explain selectivity. Difference in ion-water and water-water interactions between the resin and the solvent phases are the principle origins of anion exchange selectivity when synthetic organic exchangers are involved.

So when the organic content are increased in mixed solvent hydrated ion is squeezed out of the solution phase in to the resin phase which is comparatively having more structured water.

Thus, the study shows that the ion exchanger amberlite IRA-400 resin in nitrate form shows very good exchange potential for these oxoanions. It further increases with increase in exposed surface area, temperature and organic content in partly non-aqueous media.

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