

Equilibrium Studies on the Exchange of Halate Ions in Mixed Methanolic Solvents.

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Equilibrium studies on exchange of halate ions (ClO_3^- , BrO_3^- and IO_3^-) in aqueous methanol solvents have been performed using an anion exchanger Amberlite-IRA-400 in NO_3^- form. Conclusions have been drawn regarding the variation of free energy of the system with solvent composition at different temperatures viz., 30°, 35°, 40° and 45°C. Attempts have also been made to evaluate other thermodynamic parameters as ΔH and ΔS .

INTRODUCTION

Marcus¹ has mentioned only a few exchanges studied in mixed solvents or non-aqueous solvents. The halide ions, namely, F^- , Cl^- , Br^- and I^- have been studied against the hydroxyl form of the anion exchange resin in aqueous methanol² and aqueous ethanol³. Ions such as NO_3^- , SCN^- , CH_3SO_3^- , $\text{C}_6\text{H}_{16}\text{SO}_3^-$, $\text{C}_7\text{H}_{13}\text{SO}_3^-$ have been studied in aqueous methanol, aqueous ethanol and aqueous acetone against Cl^- ion also². A few univalent ions namely Br^- , SCN^- , ClO_4^- have been studied in DMSO against NO_3^- form of the exchanger.^{4,5} Recently Bhatnagar and Misra^{6,7} have used aqueous acetone for halate studies. Thus the halates have not been studied in aqueous alcohols. This paper deals with the anion exchange of halate ions (ClO_3^- , BrO_3^- and IO_3^-) against NO_3^- form of the exchanger Amberlite-IRA-400 in aqueous methanolic solvents.

Methanol with varying percentage with deionised water have been used under equilibrium conditions by batch process at 30°C. The selectivity coefficients are obtained graphically for evaluating the apparent equilibrium constant. The data also used to evaluate free energy of exchanges. Attempts have also been made to study the halate-nitrate exchanges at elevated temperatures i.e. 35°, 40° and 45°C also to evaluate other thermodynamic parameters.

EXPERIMENTAL

All equilibria studies have been performed by batch technique using 50 ml of

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the halate ion solution in mixed solvents (containing water and methanol on v/v basis) to provide 0, 20, 30, 40% methanol containing solvents. These were equilibrated with 1.0 gm of the resin Amberlite-IRA-400 in nitrate form in 250 ml Erlenmeyer flasks with glass stoppers. The solutions were shaken intermittently and after 24 hrs the liquid phase was analysed (after proper shaking) for the exchange of halate ion by technique already described by Bhatnagar and Mishra^{6,7} and also by Tomar *et. al.*⁸ The apparent equilibrium constant was calculated by the method of Kressman and Kitchener⁹ neglecting activities in both phases (considering the resin phase also equivalent to a dilute aqueous phase having highly ionisable NO₃⁻ ions in the fully swollen condition of the resin. The apparent equilibrium constants have been used for calculating the thermodynamic equilibrium constants using the method of graphical intergration given by Argersinger *et. al.*¹⁰. Alcohols involving hydrogen bonded structures similar to water do not change the structure of water probably up to 20%. At higher percentages there might be some changes involved. Thus in all our calculations we have calculated ln k (thermodynamic constant) as below:

$$\ln k = \int_0^1 \ln k_a dx_{BR} \quad (i)$$

From the value of ln k the free energies of anion exchange have been calculated by the following relationship:

$$\Delta F = -RT \ln k \quad (ii)$$

The results are tabulated in terms of free energy of anion exchange in Table 1.

TABLE 1

Exchange	Methanol % v/v	308 °C		313 °C		318 °C	
		K	ΔF_{cal}	K	ΔF_{cal}	K	ΔF_{cal}
ClO ₃ ⁻ -NO ₃ ⁻	0	0.1649	1103.3	0.2072	2978	0.259	853.7
	20	0.2593	826.3	0.2593	839.5	0.322	716.1
	30	0.3219	694.0	0.3961	575	0.397	583.1
	40	0.3969	567.0	0.4871	447	0.595	328.1
BrO ₃ ⁻ -NO ₃ ⁻	0	2.55	-570.8	6.69	-1182	8.98	-1387
	20	4.45	-689.2	8.98	-1366	12.5	-1596
	30	5.99	-1096.2	10.38	-1455	15.3	-1729
	40	8.98	-1344.1	12.59	-1577	18.8	-1854
IO ₃ ⁻ -NO ₃ ⁻	0	6.694	-881.84	13.17	-1713	14.7	-1698
	20	18.89	-1798.81	18.8	-1827	18.8	-1854
	30	25.27	-1977.4	28.36	-2080	32.11	-2193
	40	ppt.	—	—	—	—	—

It has also been generalised that the temperature dependence of ion exchange is not very pronounced. It is said that the enthalpy of exchange does not exceed 10 K cal/mole. Usually it is not more than 2 K cal/mole. It can be obtained by the general relationship at constant pressure,

$$\left(\frac{d \ln k}{dT}\right)_p = \frac{\Delta H}{RT^2} \quad (\text{iii})$$

As all the studies have been done at atmospheric pressure available in the room (with ± 2 atmospheres variation), ΔH can be calculated directly from this relationship or from the relationship where two different temperatures of study are involved. The $\ln k_1$ and $\ln k_2$ can be related to ΔH as below.

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{\Delta H}{R} \left(\frac{T_2 - T_1}{T_1 T_2}\right) \quad (\text{iv})$$

Other thermodynamic data like ΔS can be computed by the general relation.

$$\Delta S = \frac{\Delta H - \Delta F}{T} \quad (\text{v})$$

Duncan¹¹ and Bonner^{12,13} have calculated these parameters for a number of ion exchange systems. Very few workers have calculated these parameter for anion exchange. Table 2 mentions these values for the exchanges in question in different solvent systems.

TABLE 2

Exchange	Methanol % v/v	ΔH at 35–45°C K cal.
$\text{ClO}_3^- - \text{NO}_3^-$	0	8.7936
	20	4.2175
	30	3.6259
	40	7.8838
$\text{BrO}_3^- - \text{NO}_3^-$	0	24.5029
	20	20.1062
	30	18.2506
	40	14.3827
$\text{IO}_3^- - \text{NO}_3^-$	0	15.3104
	20	0.3740
	30	4.6523
	40	ppt

TABLE 3

Exchange	Methanol % v/v	ΔS at 35°C e.s.u.
$\text{ClO}_3^- - \text{NO}_3^-$	0	24.97
	20	11.01
	30	9.52
	40	23.75
$\text{BrO}_3^- - \text{NO}_3^-$	0	81.4
	20	67.51
	30	62.81
	40	51.06
$\text{IO}_3^- - \text{NO}_3^-$	0	52.67
	20	6.17
	30	21.52
	40	ppt

RESULTS AND DISCUSSION

It is a general practice to present the exchange of anion in terms of an equilibrium constant, it may be thermodynamic or otherwise. No doubt different authors have used different methods to evaluate this constant, however, the exchange being a reversible reaction must involve an equilibrium constant which is a measure of the selectivity of the exchanging ion for the ion in exchanger. Less workers have tried to relate the exchange with free energy of the system though the concept is useful in defining the process whether it is a chemical process or process not involving chemical changes. In actual fact the equilibrium constant is utilised for calculating the free energy of exchange also but the values might be slightly more useful as they can be used for evaluating other thermodynamic parameters also. For any chemical reaction the free energy concept of Gibbs is applicable and it is represented by F or G . When a small change takes place or a change takes place we represent the free energy change as ΔF (or ΔG). This function is equal to the net energy or the useful energy for the chemical reaction in question at constant pressure. It is defined as the difference between the total enthalpy and the energy unavailable for useful work. This unavailable energy is the product of the degree of disorder or randomness called entropy and the absolute temperature the units of entropy are evaluated as energy change per degree per mole (or calories/degree/mole). When this is multiplied by T the energy per mole associated with unavailable energy for any useful work can be obtained. In other words $\Delta F = \Delta H - T\Delta S$ where all Δ terms are for small changes in the property concerned.

The chemical change proceeds in a direction of diminution free energy content. It requires therefore, that the free energy be released from the system or ΔF is negative for the chemical reaction to take place. The chemical change requires the total bonding force in the products exceeds those in the reactants when the

total of disorder of the products is higher. It also requires that the total bonding forces of the products exceeds those of the reactants and the entropy in the product is lower but not enough to cause $T\Delta S$ to exceed ΔH . The third condition is that the total bonding force in the product are weaker than those of the reactant but the entropy increase is more but is large enough to compensate for the heat absorbed.

If we consider the data obtained for halate exchanges against nitrate ion in the anion exchanger at different temperatures we find that for $\text{ClO}_3^- - \text{NO}_3^-$ exchange ΔF values are all positive. They are showing a decrease with increasing solvent composition probably the difficult exchange becomes feasible with increasing methanol percentage. Compare to chlorate the bromate and iodate exchanges are showing negative values for ΔF . They are again showing negative increase in the values. It means that with increase in methanol concentration as ΔF values are decreasing or the exchange is facilitated for such systems.

Now this trend of exchange needs a further explanation. Usually aqueous exchanges are faster but here it appears that the exchange of the halates is

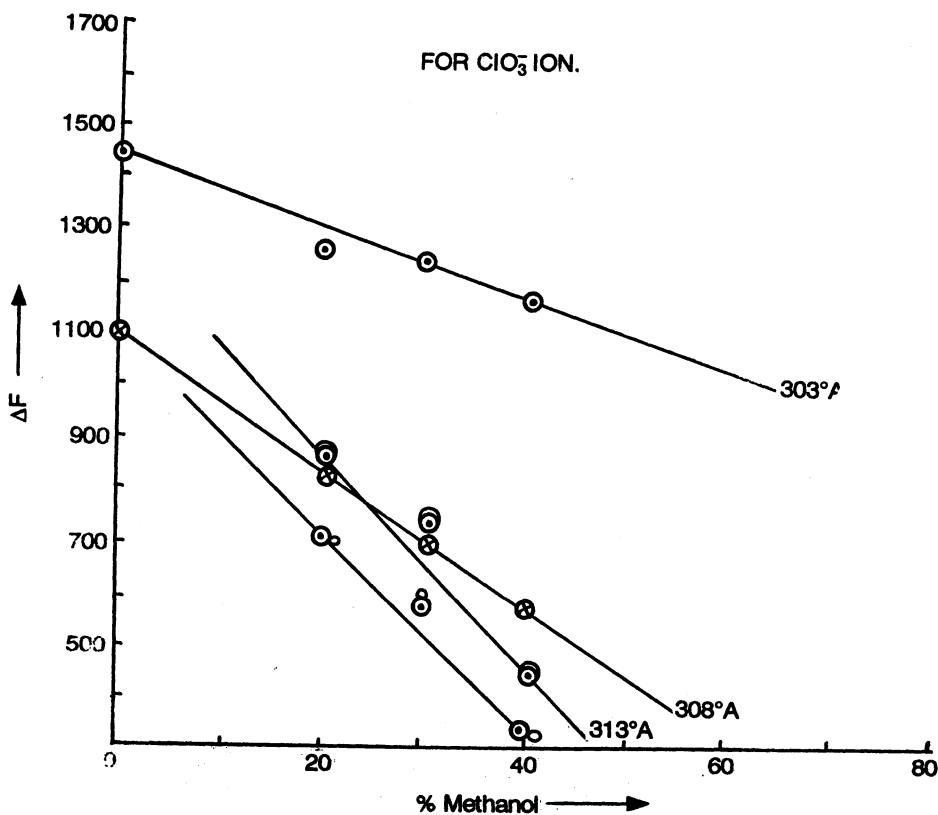


Fig. 1

increasing with increase of organic solvent. In other words these halates are pushed into the resin phase when the outer solution consists of more methanol than water. Here the suggestion given by Diamond¹⁴ can be considered profitably. In an article, Chu, Whitney and Dimond¹⁵ have made it clear that in ion exchange it is the water structure which plays an important part with the addition of the organic solvent and structure outside the resin phase as far as water is concerned is disturbed and the ions which are hydrated get dehydrated to definite extent. However, they get the same water structure inside the resin and therefore, the exchange is possible under such circumstances even with greater methanol percentage. The bigger the ion, the small is its hydrated size. If this principle is adopted we expect iodate to get exchanged more than bromate and bromate more than chlorate. Actually the sequence exchange that has been observed in different cases is as under:



A representative graph (Fig 1) for ClO_4^- is given here. The effect of the organic

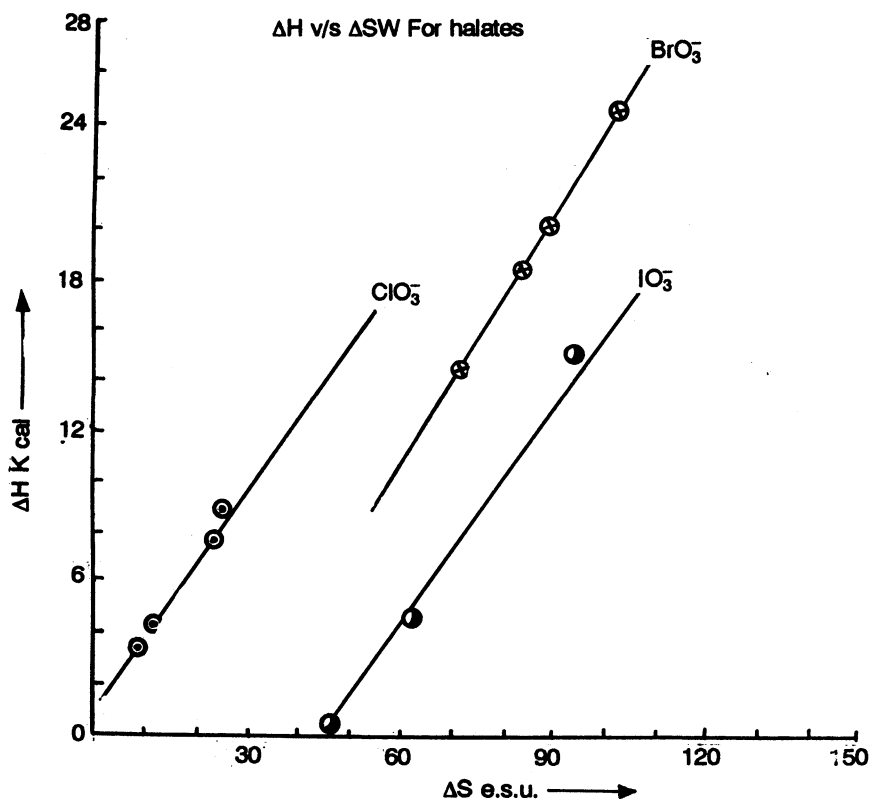


Fig. 2

solvent on exchange is thus more clear when the concept of Diamond¹⁴ and that of Chu of *et. al*¹⁵ is used.

The plots for halate ions justify the statement that with the addition of organic solvent, we expect the randomness of the system to increase at a point where the water structure is disturbed. We expect this thing to happen between 20–30% of methanolic solutions. However, the randomness is related to enthalpy hence the plots of ΔH vs ΔS are straight lines. In other words the two are interrelated which is clear from these graphs in fig. 2.

The ion exchange in all respects is just like any chemical reaction being both quantitative and reversible. However, the process will proceed in the direction in which the ions show a greater affinity. Affinity depends upon the nature of the ion, its size and valency, the nature of the resin (*i.e.* its porosity and form) and composition of the solvent in which electrolyte is dissolved. Hence the outcome of the process is dependent on all these factors. The results of these studies have thrown light on the exchange behaviour of halate ions in mixed aqueous methanolic solvents and tried to explain them.

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