Asian Journal of Chemistry Vol. 5, No. 2 (1993), 375–377

Equilibrium Studies with Chlorate Ion in Mixed Aqueous Alcohols—The Effect of Temperature

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Equilibrium studies with ClO_3^- ion in mixed solvents viz. aqueous methanol, aqueous ethanol and aqueous isopropanol have been performed using a strongly basic anion exchanger in nitrate form. Conclusions have been drawn regarding the variation of corrected selectivity coefficient with solvent composition. Effect of temperature on selectivity coefficient, variation of ΔF, ΔH, ΔS with solvent composition has also been studied.

INTRODUCTION

The chlorate ion forms a part of the halates in general and it has been studies in aqueous solution together with other halates by Avoston *et al.*[1] and Kikindai[2]. As far as organic solvents are concerned only aqueous acetone was used by Bhatnagar and Mishra[3]. Thus it is clear that aqueous alcohols have not been used so far for such studies; hence in the present work aqueous alcohols namely aqueous methanol, aqueous ethanol and aqueous isopropanol have been used to study the selectivity of chlorate ion against nitrate ion in the exchanger.

EXPERIMENTAL

Chlorate ion stock solution (0.25 m) was prepared from its potassium salt (E. Merck, 'proanalysis' quality) in double distilled water. Methanol (G.R.), ethanol (absolute ethanol of Bengal Chemicals) and isopropanol (B.D.H., A.R.) were used as organic solvents. Commercially available AR quality Amberlite-IRA-400 (Cl^-) converted to its nitrate form was used as air-dried resin. The capacity of the air-dried resin was 3.5 m mole/gm. It was a 40–60 mesh resin.

All selectivity studies were performed by the batch process. Always 50 ml of the electrolyte solution in suitable solvent system was equilibrated with exactly 1.00 gm of resin (air-dried) in nitrate form after 25 hrs and intermittent shaking during this period; the supernatant liquid was analysed for the ion exchanged from the solution. Similar studies were done to evaluate corrected selectivity constant.

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Also to see the effect of temperature, equilibrium studies were performed in methanolic solvents at four temperatures i.e. 30°C, 35°C, 40°C and 45°C in centigrade scale. From these values the other thermodynamic parameters viz. ΔF, ΔH and ΔS were also evaluated. Equations used are

$$\Delta F = -RT \log K$$

$$\Delta H = \frac{2.303\ RT_1 \log K_2}{T_2 - T_1}$$

and

$$\Delta S = \frac{\Delta H - \Delta F}{T}$$

These were evaluated at all the methanolic concentrations.

RESULTS AND DISCUSSION

The results of these studies presented graphically indicate the trends as shown below:

(1) The correct selectivity coefficients for ClO_3^-/NO_3^- exchange vary with alcohol percentges (v/v). It is seen that the selectivity of the ion increases with alcohol per centage from 0 to 40% (v/v). This is seen at all anionic concentrations from 0.02 to 0.1 m.

(2) Plot of log K *vs* 1/T shows a linear decrease *i.e.* the selectivity of chlorate ion increases with increase in temperature at all methanol per centages from 0 to 40% (v/v).

(3) Graph of ΔF per centage of methanol shows that selectivity increases with increase in methanol per centage.

(4) Graph shows the plot of ΔH *vs* per centage of methanol. It is seen that between 10–20% selectivity increases with increase in per centage of alcohol; then it decreases with further increase in alcohol per centage.

(5) Graph of ΔS vs per centage of methanol shows the same trend as that of ΔH vs per centage of methanol.

(6) Plot of ΔH vs ΔS shows linear increase.

Increased exchange for ClO_3^-/NO_3^- in increasing alcohol per centage can be explained by the theory of water structure given by Diamond and Whitney[4].

It is said that bigger the naked ionic size of the ion, lesser is its hydrated ionic size. The control Cl atom being bigger than the central N atom in NO_3^- ion, hence the hydrated NO_3^- ion will be bigger than the hydrated ClO_3^- ion, hence the hydrated ClO_3^- shows more exchange. When the per centage of alcohol in the outside solution is increased, it becomes less and less water containing but the water in the pores of resin remains as it is. Hence with increased alcohol per centage ClO_3^- prefers resin phase where it gets more water for hydration and gets exchanged; thus the selectivity of ion also increases with alcohol per centage. Also it is seen that the order of selectivity for ClO_3^- ion exchange in the three alcohols is;

isopropanol > ethanol > methanol

When also confers that as the outside solution becomes more and more nonpolar, ClO_3^- prefers the resin phase where it gets more polar water for hydration that the outside solution. As the temperature is increased the randomness of ClO_3^- ion in the solution increases and more and more ions are available at the exchange site of the resin and hence more ions are exchanged. Thus the selectivity of ClO_3^- ion increases with temperature.

ΔF Decreases with increase of organic solvent in the system. In other words the exchange is facilitated by increase in alcohol concentration in the external solution. Graphs of ΔH vs per centage of methanol and ΔS *vs.* per centage of methanol show that ΔH and ΔS show decrease up to 20% methanol concentration because here the water structure is not much disturbed as compared to 30 to 40% methanol where the values show increase. Also from the graph of ΔH *vs.* ΔS, which shows a linear increase, it is clear that the enthalpy change in each case and the randomness of the system is related to the enthalpy change of the system.

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(*Received*: 10 October 1991; *Accepted*: 10 July 1992) AJC–448