Ion-Exchange Rate of Chromate and Dichromate Ions on Bis(triethylamine)zirconium

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Synopsis. Kinetic studies of $K_2Cr_2O_7$ and K_2CrO_4 have been performed on an inorganic anion exchanger, bis(triethylamine)zirconium in Cl^- form. F values have been determined at four different temperatures 30, 40, 50, and 60 °C with ±1 °C variation and corresponding Bt values are evaluated and plotted as a function of temperature. The mechanism is found to be particle diffusion control. Various parameters viz. effective diffusion coefficient (D_i), diffusion coefficient (D_o), energy of activation (E_a), and entropy of activation (ΔS^*) have been evaluated.

Some studies on kinetics of ion exchange on inorganic ion exchangers have been reported.[1-9] The present report summarizes the kinetic studies for ion-exchange rate of chromate and dichromate ions on bis-(triethylamine)zirconium. Experimental and theoretical approaches have been used to show that the rate determining step is the diffusion through the particles. The energy of activation and other parameters are calculated.

Experimental

Synthesis of Ion-Exchange Material. Bis(triethylamine)-zirconium was prepared by mixing 0.1 M† zirconium dichloride oxide and 0.1 M triethylamine solution in the volume ratio of 1:2. After 24 h it was filtered, washed and dried in an incubator at 40±1 °C. The product was then broken down into small particles by immersing in water. Exchanger was kept in 1.0 M NaCl solution to convert it in chloride form. It was then washed and dried again at 40±1 °C.

Kinetic Measurements. Limited bath technique was applied to perform the kinetic measurements. The exchanger was finely ground and sieved into particles of different mesh sizes (30—50, 50—100, and 100—150) by using the U.S. standard mesh sieves. In all the cases studied, particles of 50—100 mesh were used, unless otherwise stated. In stoppered conical flasks 4 ml of standard anionic solutions of 0.02 M were shaken with exchanger (0.2 g) in a temperature controlled shaker (Sew India) at various temperatures at a frequency of 120 RPM. The pH of 0.02 M $K_2Cr_2O_7$ solution was 4.6 and that of K_2CrO_4, 8.2. After appropriate intervals of time, the solutions were filtered through Whatman No. 42 filter paper. The amount of $Cr_2O_7^{2-}$ and CrO_4^{2-} ions were determined iodometrically.[10] Kinetic experiments were performed at 30, 40, 50, and 60 °C with ±1 °C variation. Interruption test was performed in the similar way at 30 °C. After 20 min the solutions were separated from the exchanger and reimmersed after 10 min. The metal ion contents were determined at different intervals of time.

Results and Discussion

Interruption test for $Cr_2O_7^{2-}$ ion was used as an experimental test to decide whether the kinetics is controlled by film diffusion or particle diffusion. The results of interruption test (Fig. 1) show that rate of exchange increases after 10 min interruption. This indicates that mechanism should be particle diffusion. This is because the concentration gradients disappear in the particle during the interruption and are much greater than before at the surface.

Equations developed by Boyd et al.[11] and improved by Reichenberg[12] were used to obtain kinetic parameters. F values at different time intervals and temperatures were obtained for $Cr_2O_7^{2-}$-Cl^- exchange and plotted in Fig. 2. These results show that the rate of exchange increases with temperature. The uptake of ion is rapid initially but it decreases with the elapse of time. Similar behavior was shown by CrO_4^{2-} ion.

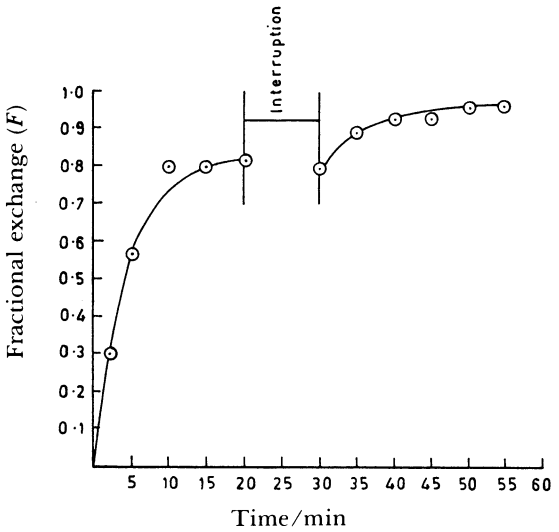

Fig. 1. Effect of an interruption test on the rate of $Cr_2O_7^{2-}$-Cl^- exchange on zirconium bis(triethylamine) at 30 °C.

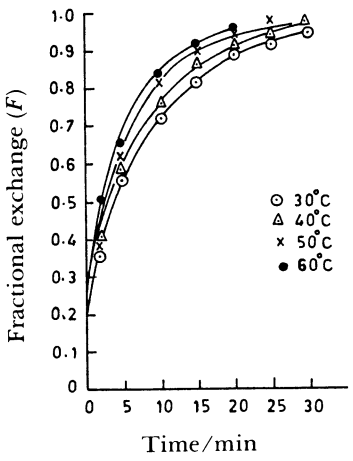

Fig. 2. Rate of exchange of $Cr_2O_7^{2-}$ at different temperatures on zirconium bis(triethylamine).

† 1M=1 mol dm^{-3}.

$$F = \frac{\text{amount of exchange after time } t}{\text{amount of exchange after infinite time (equil.)}}$$

For the limited bath technique the equations developed by Boyd et al.[11] can be used here

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 Bt), \quad (1)$$

where $$B = \frac{\pi^2 D_i}{\gamma^2}. \quad (2)$$

D_i is the effective diffusion coefficient, γ is the radius of the particle. Bt values were evaluated from the F values from the table of Reichenberg.[12] A typical Bt vs. t plot for $Cr_2O_7^{2-}$ ion (Fig. 3) at four different temperatures indicates that the plots are straight lines passing through the origin. The results confirm that the rate determining step is diffusion through the particle.

The particle size also has a marked influence on the rate of exchange which can be shown by the Bt vs. t plot for $Cr_2O_7^{2-}$ ion for three different particle radii at 40±1 °C (Fig. 4). The rate of exchange is inversely proportional to the square of the particle radius (Fig 5). The radius of the particles was calculated by the mesh size using the conversion table.[13] For this purpose the lower limit mesh corresponding to higher limit radius was taken instead of taking a mean radius. The higher limit radius was considered by keeping the view of slight swelling of the exchanger particles.

Equation 2 was used for the calculation of D_i. A linear relationship was obtained on plotting log D_o against T^{-1}/K (Fig. 6) assuming the Arrhenius equation

$$D_i = D_o \exp(-E_a/RT). \quad (3)$$

On extrapolating the plot of log D_i against T^{-1}/K, log

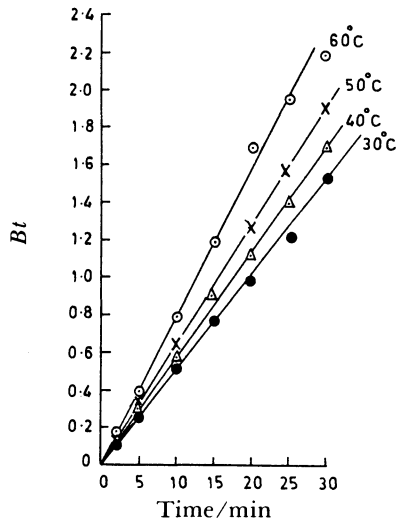

Fig. 3. Influence of temperature on the rate of exchange for $Cr_2O_7^{2-}$ ion using zirconium bis(triethylamine) r=0.015 cm.

Table 1. Diffusion Coefficient, D_o, Energy of Activation, E_a and Entropy of Activation, ΔS^*, of $Cr_2O_7^{2-}$ Ions on Bis(triethylamine)zirconium in Cl^- Form

Migrating ion	D_o	E_a	ΔS^*
	$m^2\,s^{-1}$	$kJ^{-1}\,mol^{-1}$	$J\,K^{-1}\,mol^{-1}$
$Cr_2O_7^{2-}$	5.01×10^{-7}	25.42	−25.72
CrO_4^{2-}	5.01×10^{-7}	23.89	−25.72

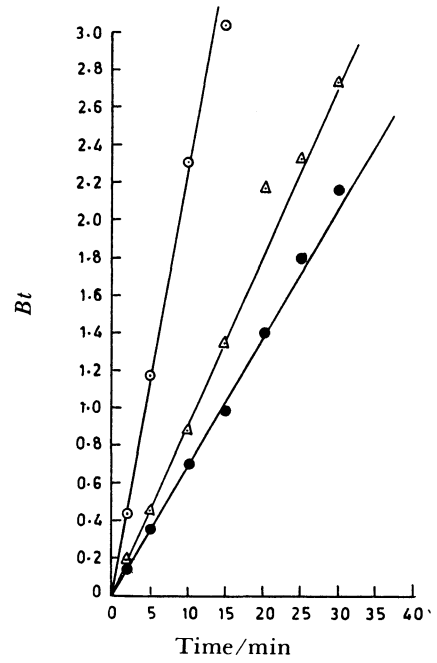

Fig. 4. Effect of particle size on the rate of exchange for $Cr_2O_7^{2-}$-Cl^- on zirconium bis(triethylamine). △ 0.015 cm, ● 0.030 cm, ⊙ 0.0075 cm.

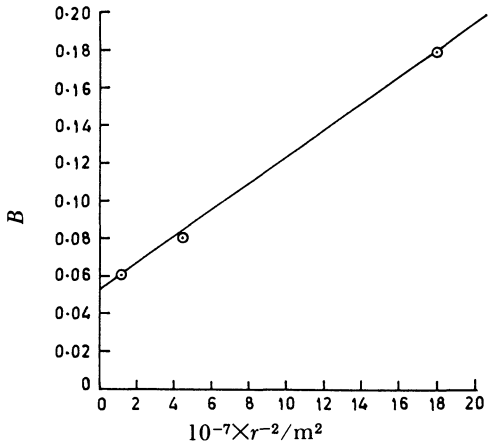

Fig. 5. Plots of B vs. r^{-2} for $Cr_2O_7^{2-}$ at 40 °C.

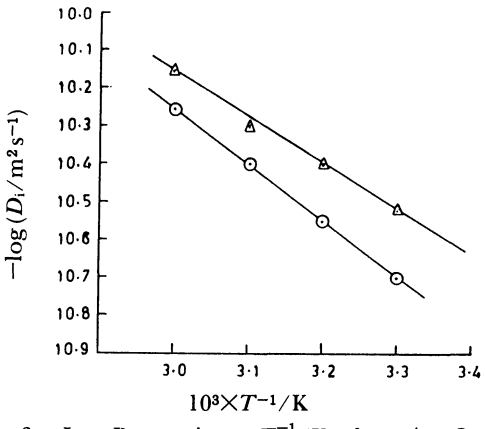

Fig. 6. Log D_i against T^{-1}/K for △ $Cr_2O_7^{2-}$, ⊙ CrO_4^{2-}.

D_o values are calculated. Substitution of these values in the following equation gives entropy of activation, ΔS^*

$$D_o = 2.72\, d^2\, KT/h \exp(\Delta S^*/R) \quad (4)$$

where d is the ionic jump distance assumed equal to 5×10^{-10} m (1), K the Boltzman constant, h Planck's constant, and R the gas constant. The values of E_a, D_o, and ΔS^* are given in Table 1.

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