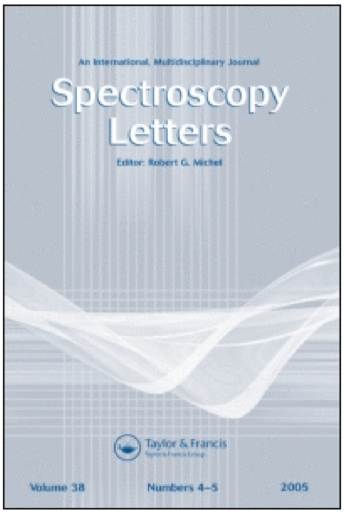

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Isotopic Exchange Between Barium Oxalate and Barium Ion in Aqueous Solution

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ISOTOPIC EXCHANGE BETWEEN BARIUM OXALATE AND BARIUM ION IN AQUEOUS SOLUTION

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ABSTRACT

The heterogeneous isotopic exchange reaction of precipitated barium oxalate in barium chloride solution has been studied using Ba-133 as tracer. The effect of barium chloride concentration on the rate of isotopic exchange reaction has been studied. It was found that the rate was controlled by surface mass reaction and particle diffusion process in the solid particle. The result also indicate that the effect of recrystallization can be neglected.

INTRODUCTION

The heterogeneous exchange reaction between a solid phase and a solution can be described by the following equation:

$$A^{*}X(s) + AY(l) \rightleftharpoons AX(s) + A^{*}Y(l)$$

Ions or atoms A are exchanged on the surface of the AX. In solid liquid heterogeneous isotopic exchange reactions, there is a rapid exchange at the initial of the reaction between the surface of the solid and the solution. This initial reaction is then followed by the relatively slower process of incorporation of surface metarial into the body of the latlice by particle diffusion and recristallization . The initial exchange depends on the surface area of the crystal, while subsequent processes are controlled by particle size, crystal perfection, solubility and temperature. The total exchange may thus be regarded as composed of an exchange reaction at interface of the crystal, diffussion into the interior of the crystal and recrystallization. The over-all rate will depend not only on the rate of exchange of radioactive atoms at the interface but also on the rate at which the adsorbed material is incorporated in the interior of the crystal by means of self-diffusion and,or recrystallisation. For example the rate of the exchange reaction of the system $CaC_2O_4(s)-Ca^{2+}(aq)$ is controlled by the super pozition of a faster interfacial ion exchange process and slower interparticle diffusion process[1] . It is found that the surface mass reaction in the systems $BaSO_4(s)-Ba^{2+}(aq)$,$SrSO_4(s)-Sr^{2+}(aq)$ was rate determining step of the exchange reaction[2]. Surface mass reaction and recrystallization in the system $CaCO_3(s)-Ca^{2+}(aq)$ played the most important roles[3] .

In this study the kinetics and mechanizm of the heterogeneous isotopic exchange reaction of barium oxalate and barium ion in solution were studied. The radioisotope Ba-133 was used to measure the concentration change during the reaction. The effect of barium chloride concentration for a different mole ratio of the exchanging ions on the solid surface and in the solution was studied.

EXPERIMENTAL

The barium oxalate used in this work was obtained from precipitation of equimolar amounts of 0.1 M solutions of pure amonium oxalate and barium chloride(Merck)at 30°C. During precipitation the mixture was continuously stirred with a mechanical stirrer. After this treatment the precipitate and the mother liquid was kept at 30°C for 24 hours, then the liquid was decanted. The precipitate was washed with alcohol and ether and dried at 105°C.

Barium-133 tracer was high-purity, aqueous solution was obtained from the Radiochemical Centre-Amersham. The radioactive solution involved 5 µg barium in ml was added to the inactive barium chlorid solutions at different concentrations. The concentrations of barium chloride solution for these experiments are 0.025, 0.033, 0.050, 0.1 and 0.2 M. In each experiment 10 ml radioactive barium chloride solution was added to the 0.225 gram of barium oxalate specimens and were stirred for 1, 5, 15, 30 and 60 minutes at 25°C. Then the suspension was centrifuged, decanted and the counting rate of the supernatant liquid was determined and compared with that of a standard solution.

The gamma ray measurements were carried out by a multichannel analyzer (Canberra 8160/e) with scintillation detector (NaI - Tl).

RESULTS AND DISCUSSION

For solid liquid heterogeneous systems when the tracer is present in solution the isotopic exchange fraction is calculated as follows :

$$F = \frac{I_o - I}{I_o}$$

Where F denotes the exchange fraction, I_o and I show the initial counting rate of the solution and the counting rate at the time t respectively.

The measured exchange fractions, during the experiments are shown in Fig.1 . As it is seen that the exchange fraction increases much faster for lower concentrations then higher ones. The time required to achieve equilibrium is olso shorter for lower concentration. The exchange fraction at equilibrium is olso higher in the dilute solution than in concentrated ones.

The rate constants of the isotopic exchange reactions were calculated according to the Mc. Kay equation[4]

$$k = - \frac{ab}{a+b} \cdot \frac{1}{t} \ln(1-F)$$

Where a and b are the g.atoms/l of the reactans in each two phases.

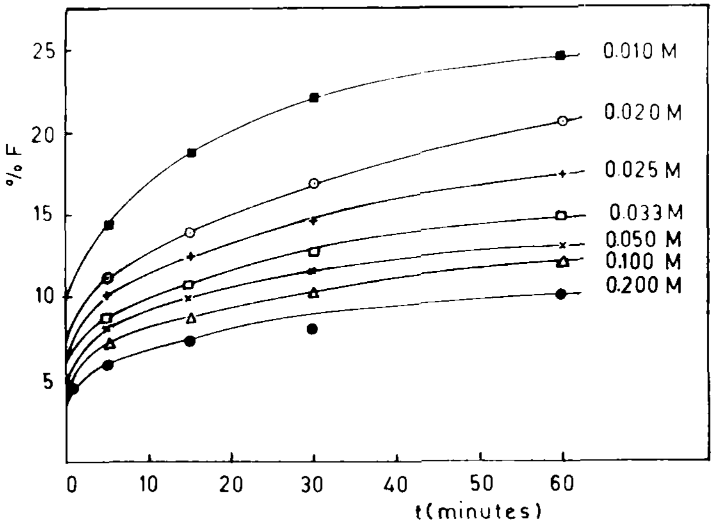

Figure 1 . Exchange fractions vs. reaction time in various Barium chloride concentrations.

Values of ln(1-F) as a function of reaction time at each concentrations are plotted in Fig.2 . The resulting curves are similar to those of independetly decaying activities, indicating the non homogeneous nature of the exchange reaction. In order to analyse the curve the final linear portion was extrapolated back to t=0, and on subtracting the extrapolated line from the original curve, another straight line is obtained which represents the initial reaction. The ower-all exchange is thus seen to consist of a fast initial precess followed by a relatively slower process which completes the exchange. It is,

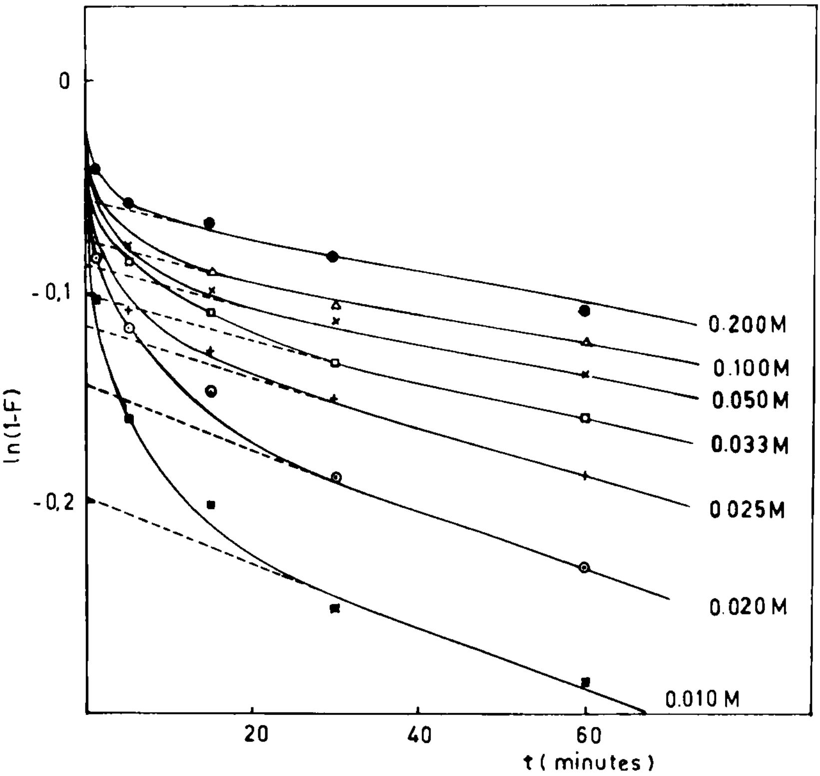

Figure 2 . ln(1-F) versus reaction time in various barium chloride concentrations.

however, possible that there may be other contributing reactions which are resolved by this analysis.

The rate constants for initial fast reaction are determined at each concentration from the exchange half-times of the lines using the following equation :

$$k = -\frac{ab}{a+b}\,\frac{1}{t}\ln\frac{1-F'}{1-F^{o}}$$

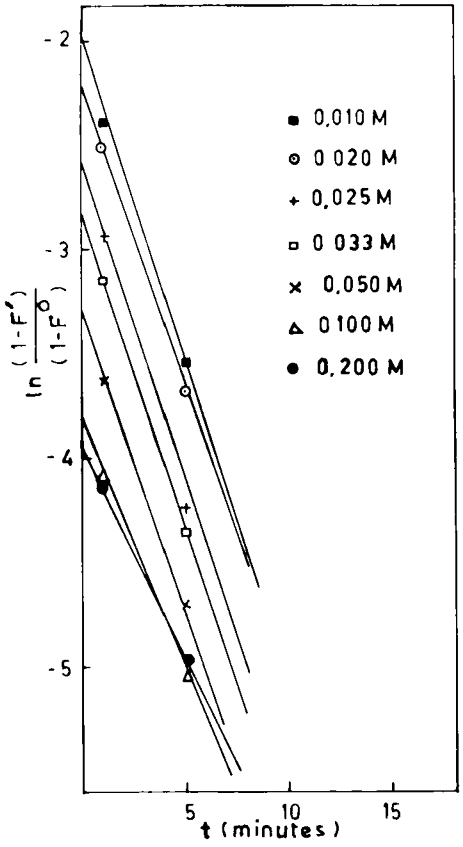

Figure 3 . ln $\frac{(1-F')}{(1-F^{o})}$ versus reaction time in various barium chloride concentrations.

Where F' and F^{o} are exchange fractions and apparent exchange fraction at the extropolated straight line respectively (Fig.3) .

The rate constants and exchange half-times for both reactions are shown in table 1.

Table 1: Effect of concentration on rate constant

Concentration of $BaCl_2$(M)	Exchange Half-Time Step I $t_{1/2}$ sec.	Step II $t_{1/2}.10^{-3}$ sec.	Rate Constant atom $gram^{-1}$ sec^{-1} $k.10^4$	$k.10^7$
0.010	60	28.86	1.04	2.18
0.020	60	34.62	1.92	3.33
0.025	60	40.38	2.31	3.44
0.033	60	41.58	2.86	4.13
0.050	60	51.60	3.84	4.44
0.100	72	51.96	4.81	6.00
0.200	90	51.96	5.13	8.00

In all cases, the first step of the exchange reaction is more rapid than the second ones. From the above discusion, it can be concluded that the exchange reaction begins with mass reaction. Then the particle diffusion takes place in the second step of the reaction[3] .

If the rate of the particle diffusion very slow and effect of the recrystallisation process is neglible, then the ratio of the total amount of material in the solution to those on the surface at equilibrium. Thus we can obtain the

Table II: Exchange ratio of barium oxalates at different barium chloride concentrations.

Concentration of $BaCl_2$(M)	$(a/b)_A$	$(a/b)_B$	$(a/b)_A/(a/b)_B$
0.010	0.221	10	0.022
0.020	0.160	5	0.032
0.025	0.123	4	0.030
0.033	0.112	3	0.037
0.050	0.094	2	0.047
0.100	0.083	1	0.083
0.200	0.061	0.5	0.122

following relation :

$$\left(\frac{a}{b}\right)_A = \frac{I_o - I_\infty}{I_\infty}$$

If the effect of the recrystallisation process is not neglible the following relation is valid :

$$\left(\frac{a}{b}\right)_B = \frac{W}{C_L . V . M}$$

a and b represent the moles of exchanging ions on the solid surface and in the solution. W denotes the weight of barium oxalate, C_L is the concentration of barium chloride solution and V is the volume of the solution. As it is seen from table II the experimental values of $(a/b)_A/(a/b)_B$ are less than unity.

Physically, the value of $(a/b)_A/(a/b)_B$ represent the exchangable ratio of the exchange reaction. The small value of this ratio implies that the particle diffusion proces is very slow, and is not important compared with the mass exchange reaction at the interface[1] . On the other hand, this ratio is a measure of the extent of recrystallization on the solid surface during an experiment. If the effect of the recrystallization on the exchange reaction is not important, then this ratio should be much less than unity. As can be seen from table II the ratio increases as the concentration of the solution increases. However, the value of $(a/b)_A/(a/b)_B$ should be unit at infinite time. Although the above result olso indicates that the extent of recrystallization is not large, but the recrystallization is still a predominant proces in the mass exchange reaction.

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