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ISOTOPIC EXCHANGE REACTION BETWEEN BARIUM ION AND TRI BARIUM PHOSPHATE

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ABSTRACT

Heterogeneous exchange reaction of tri barium phosphate in barium chloride solution has been studied using ^{133}Ba as a tracer. The results show that the exchange fraction increases as barium chloride concentration increases for different mole ratio of the exchange ion on the solid surface and in the solution. The phenomenon was studied with respect to the previous treatment of the precipitate leading to different crystal sizes and the effect of reaction time.

ÖZET

Tri baryum fosfat ile baryum klorür çözeltisi arasındaki heterojen izotop değiştirme reaksiyonu izleyici olarak ^{133}Ba kullanılarak incelendi. Katının yüzeyi ile çözelti arasında değiştirilen iyonların farklı mol oranları için, izotop değiştirme fraksiyonunun, baryum klorür konsantrasyonu ile arttığı görüldü. Çökeltinin hazırlanışı sırasında kristal büyüklüğünü etkileyen işlemin ve reaksiyon süresinin, değiştirme fraksiyonuna etkisi incelendi.

INTRODUCTION

Heterogeneous isotopic exchange reactions have been investigated in various systems /1-7/. For many heterogeneous isotopic exchange reactions it has been found that there is an initial relatively rapid exchange between the surface of the solid and the solution. This initial reaction is then followed by the relatively slow process of incorporation of surface material into the body of the lattice by self-diffusion and recrystallization. The extent of the initial rapid exchange depends on various factors.

In this work the isotopic exchange reaction between tri barium phosphate and barium ions in solution was studied. The radioisotope ^{133}Ba used to measure the concentration change during the reaction. In previous studies /8-12/ the isotopic exchange reaction of the system $Ca_3(PO_4)_2$ (s)/Ca^{2+}(aq) have been investigated. As there are no detailed investigations concerning the effect of solution concentration, in our study we have investigated especially the effect of solution concentration for a fixed mole ratio of the radioactive barium ions to the inactive barium ions in the solution. On the other hand it has been found that the rate of isotopic exchange in the system $CaCO_3$(s) / Ca^{2+}(aq) /13/ increases as $CaCl_2$ concentration decreases; but the exchange % in the system $Ca_3(PO_4)_2$ (s) / Ca^{2+}(aq) /11-12/ increases as $CaCl_2$ concentration increases. This difference is due to the method of calculation. If the specific activities are used in the calculation, the exchange rate increases as the solution concentration increases, on the other hand if only counting rates are used in the calculation, the exchange rate increases as the solution concentration decreases. In this study specific activities were used in calculations. In addition to the effect of the solution concentration studies, experiments were performed to determine the effect of the particle size of the product and the effect of the reaction time.

EXPERIMENTAL

Tri barium phosphate used in this work was obtained from precipitation of equimolar amounts of 0.1 M solutions of pure tri sodium phosphate and barium chloride (Merck) at 60°C. During precipitation the mixture was continuously stirred with a mechanical stirrer. After this treatment the precipitate and the mother liquid was kept at 60°C for 24 hours,then the liquid was decanted. The precipitate was washed with alcohol and ether and dried at 110°C.

The ^{133}Ba tracer was a high-purity, aqueous solution obtained from the Radiochemical Centre-Amersham. The standardized radioactive solution was added to the inactive barium chloride solutions at different concentrations. In each experiment 10 ml $BaCl_2$ solution of known concentration was added to the equal amount of $Ba_3(PO_4)_2$ samples at 22°C and were stirred for one hour. Then the suspension was centrifuged, decanted and the counting rate of the suparnatant liquid was determined and compared with that of a standard solution.

The gamma ray measurements were carried out by a multichannel analyzer (Canberra 8100/e) with scintillation detector (NaI-Tl). The exchange fraction % was calculated as follows;

$$P\ (\%) = \frac{As\ S}{As\ T} \times 100$$

Where P denotes the exchange fraction, As S and As T shows the specific activity of the solid and the standard solution respectively.

RESULTS AND DISCUSSION

Effect of $BaCl_2$ Concentration

a) $BaCl_2$ solutions at different concentrations were prepared at a fixed mole ratio of $Ba^{2+}/\overset{*}{B}a^{2+}$. The barium content of $Ba_3(PO_4)_2$ samples were equivalent to the amounts of barium in 10 ml 0.1 M $BaCl_2$ solution. Results which are given in Table-1 shows that the exchange fraction % increases as $BaCl_2$ concentration increases.

TABLE-1. Exchange fraction % of $Ba_3(PO_4)_2$ in various $BaCl_2$ concentrations at 20°C (0.2006 g sample per 10 ml $BaCl_2$ Solutions; $Ba^{2+}/\overset{*}{B}a^{2+} = 2.7 \times 10^5$).

Concentration of $BaCl_2$(M) x 10^3	$\frac{n_S}{n_L}$	Exchange Fraction % I	II
10	10	1.09	1.00
20	5	1.16	1.09
25	4	1.80	1.40
33	3	1.98	2.03
50	2	2.81	2.83
100	1	4.74	4.70

Changing ions in the solution and on the solid surface are represented by n_L and n_S respectively.

b) The $Ba^{2+}/\overset{*}{B}a^{2+}$ ratio was changed by adding equal amounts of radioactive $BaCl_2$ solutions to the inactive $BaCl_2$ solutions at various concentrations. As it is seen in Table-2 the increase in the exchange fraction is more than the ones given in Table-1. By preparing $\overset{*}{B}aCl_2$ solutions having the same radioactivity, the experimental errors can be kept at low limits.

TABLE-2. Exchange fraction % of $Ba_3(PO_4)_2$ in various $BaCl_2$ concentrations at 20°C (0.2006 g sample per 10 ml $BaCl_2$ solution).

Concentration of $BaCl_2$(M) x 10^3	$\frac{n_S}{n_L}$	Exchange Fraction % I	II	$Ba^{2+}/\overset{*}{Ba}^{2+}$ x 10^{-6}
10	10	2.12	1.76	0.10
20	5	3.05	3.02	0.21
25	4	3.01	2.45	0.27
33	3	4.68	4.46	0.36
50	2	6.37	5.03	0.54
100	1	7.68	7.09	1.09

On the other hand, with respect to exchange equilibrium, keeping the ratio of $Ba^{2+}/\overset{*}{Ba}^{2+}$ constant is more suitable.

Effect of $Ba_3(PO_4)_2$ Preparation

$Ba_3(PO_4)_2$ was prepared by stirring the mother liquid for two hours after the precipitation process. The rest of the procedure was described previously. Different treatment of the precipitates which could change the crystal size by recrystallization should have influence on the exchange fraction. This can be expected since the particle size, in the case of stirred precipitate must be very small in comparison with that of a fresh precipitate. As it is seen in Table-3, the exchange fraction shows a higher increase in comparison with that of the fresh precipitate (Table-1).

TABLE-3. Effect of condition of preparation of $Ba_3(PO_4)_2$ on exchange fraction % at 20° (0.2006 g sample per 10 ml $BaCl_2$ solution; $Ba^{2+}/\overset{*}{Ba}^{2+} = 2.7 \times 10^5$).

Concentration of $BaCl_2$(M) x 10^3	$\frac{n_S}{n_L}$	Exchange Fraction % I	II
10	10	1.24	1.40
20	5	2.26	2.70
25	4	2.61	2.73
33	3	3.43	3.64
50	2	4.12	4.33
100	1	6.18	7.54

The exchange fraction depends on the specific surface of the solid particles /3/. As the total exchange in the surface area of the smaller solid particles is larger, above conclusion is strengthened by these results.

Effect of Reaction Time

The experiment were carried out for 0.05 M $BaCl_2$ solutions and equal amounts of $Ba_3(PO_4)_2$ samples. As shown in Table-4 there is a rapid exchange at the beginning of the reaction. This initial reaction is then followed by the slow process. 60 % of total exchange is attained in first five minutes. The rapid exchange at the beginning of the reaction occurs on the surface of the solid particles. Following this reaction there is a slow process due to self-diffusion and recrystalization in which the adsorbed material is incorporated in to the solid.

TABLE-4. Effect of reaction time on exchange fraction (0.2006 g sample per 10 ml 0.05 M $BaCl_2$ solution; $Ba^{2+}/\bar{B}a^{2+} = 2.7 \times 10^5$).

Time (min)	Exchange Fraction % I	II
1	0.86	1.05
3	1.26	1.39
5	1.38	1.46
15	1.90	1.65
30	2.02	1.92
60	2.53	2.22

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