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# KINETICS OF EXCHANGE REACTIONS IN A CATION-EXCHANGE RESIN

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## ABSTRACT

The kinetics of the exchange reactions of several cations from aqueous solution by protons from a sulfonated polystyrene resin have been studied in detail. The reaction rate is first-order with respect to both the resin and the cation concentrations and increases with the stirring velocity. The activation parameters for the exchange of $Mg^{2+}$, $Cu^{2+}$, $Cr^{3+}$, and $Fe^{3+}$ ions have been determined. A $\Delta H_{\ddagger}{}^{\circ}$ vs $\Delta S_{\ddagger}{}^{\circ}$ plot for these reactions is linear, yielding an isokinetic temperature of 333 K. The rate of reaction appears to increase with increasing ionic radius and to decrease with increasing electrostatic charge of the cation to be exchanged. The rate-controlling step seems to be diffusion through the aqueous layer surrounding the resin particles.

## INTRODUCTION

Ion-exchange resins have extensive applications in water treatment, in purification, in trace-elements recovery, and as an alternative to conventional chromatography for separation of the components of a mixture, besides being

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also useful for biological and medical purposes and in the preparation of pharmaceuticals [1, 2].

Thus, it is only natural that the kinetics of ion-exchange reactions have received considerable attention from both theoretical [3-8] and experimental [9-18] perspectives. The thermochemical aspects of these reactions have also been contemplated [19-22].

Recently, the kinetic results concerning the exchange reactions of potassium [23] and chloride [24] ions in a sulfonated polystyrene resin have been reported. A systematic study of the kinetics of exchange of several cations from aqueous solution by protons from a resin of the same type has now been undertaken and the results are reported here and discussed in detail.

## EXPERIMENTAL

The solvent used in all the experiments was water previously treated by double distillation followed of demineralization by means of both a cation-exchange resin and an anion-exchange resin. The average specific conductivity of the water thus purified was 0.9 $\mu$S/cm.

The resin was Lewatit-S1080 (Merck), of the sulfonated polystyrene type, commercially available in spheres of 0.2-0.3 mm diameter and as the sodium salt. The protonated form of this resin was obtained by treating it with 1 *M* HCl solution.

The exchange capacity of the resin was determined to be 4.13, 3.28, and 1.38 meq/g of dry resin for $K^+$, $Cu^{2+}$, and $Al^{3+}$ ions, respectively. Therefore, it clearly decreases as the electrostatic charge of the cation to be exchanged increases.

The salts used in the experiments were of analytical reagent quality (Merck and Panreac).

The kinetics were followed by monitoring the decrease in the pH of the solutions by means of a Radiometer pH-meter 26 provided with a combination electrode. The initial pH was adjusted within the 3-4 interval by addition of very dilute HCl solution.

In a typical experiment, 800 mL of an aqueous solution of $CuSO_4$ (1.25 meq/L) contained in a 1-L beaker was put in a conventional thermostat at 25.0°C. A thermometer and a paddle stirrer, as well as the combination electrode, were then introduced in the beaker. The stirrer was connected to a rheostat calibrated in arbitrary units (a.u.) so that the stirring velocity could be controlled. Once thermal equilibrium had been attained, 1 g of dry resin was added to the solution, and the progress of the exchange reaction was followed by means of the potentiometric technique described above.

## RESULTS

The initial rates for the $Cu^{2+}$-$H^+$ exchange reaction at several resin concentrations, all the other conditions kept constant, were determined and are listed in Table 1. We can see that the initial rate is directly proportional to the resin concentration; i.e., the reaction is first-order with respect to the resin.

Double logarithmic plots of the initial rate against the cation concentration for exchange of $Fe^{3+}$, $Cr^{3+}$, and $Cu^{2+}$ ions by protons from the resin are linear (see Fig. 1), the slope being nearly unity. It can be inferred that the reaction rate is also first-order with respect to the cation concentration.

From the kinetic run in Table 2, *F*, the fractional attainment of equilibrium, can be derived as the ratio between the proton activities at time *t* and at the end of the reaction:

$$F = a[H^+]_t / a[H^+]_\infty \tag{1}$$

Table 2 shows that $-\ln(1 - F)$ remains directly proportional to the time variable throughout the reaction, thus allowing the slope, *R*, of the relationship to be obtained [25]:

$$-\ln(1 - F) = Rt \tag{2}$$

The *R* parameter for the exchange reactions of $Cu^{2+}$, $Cr^{3+}$, and $Fe^{3+}$ ions increases linearly with the stirring velocity (see Fig. 2).

TABLE 1. Dependence of the Initial Rate of the $Cu^{2+}$-$H^+$ Exchange Reaction on the Resin Concentration[a]

| [Resin], g/L | $10^6\ r_i$, mol/L·s)[b] | $10^6\ r_i$/[Resin], mol/(g·s) |
|---|---|---|
| 0.94 | 1.07 | 1.14 |
| 1.25 | 1.47 | 1.18 |
| 1.56 | 1.79 | 1.15 |
| 1.88 | 2.04 | 1.09 |
| 2.19 | 2.45 | 1.12 |

[a] $[CuSO_4]$ = 0.625 meq/L, temperature 25.0°C, stirring velocity 30 a.u.
[b] Initial rate.

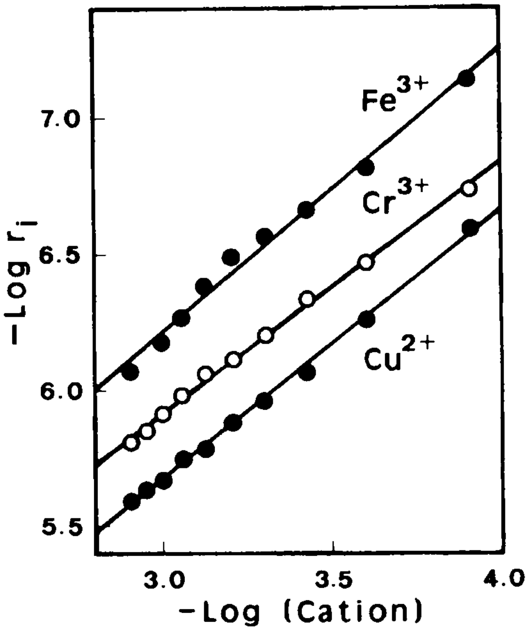

FIG. 1. Dependence of the initial rate (in mol/(L·s)) on the cation concentration (in eq/L) for the $Fe^{3+}$-$H^+$ (slope = 1.04, $r$ = 0.994), $Cr^{3+}$-$H^+$ (slope = 0.93, $r$ = 0.998), and $Cu^{2+}$-$H^+$ (slope = 0.99, $r$ = 0.998) exchange reactions. [Resin] = 1.25 g/L, temperature 25°C, stirring velocity 30 a.u.

The second-order rate constants for these reactions were also obtained. They fit the Arrhenius equation as can be seen in Fig. 3.

The activation parameters are collected in Table 3. The maximum possible errors for the enthalpies and entropies of activation were estimated by the method of Petersen et al. [26] and appear in Table 4.

A $\Delta H_{\ddagger}{}^{\circ}$ vs. $\Delta S_{\ddagger}{}^{\circ}$ plot for the four exchange reactions is linear (Fig. 4). From the slope of that plot, an isokinetic temperature of 333 K can be deduced.

Finally, the second-order rate constants for the exchange of several monovalent, divalent, and trivalent cations were determined for the same experimental conditions (Table 5). Since the number of protons from the resin liberated by each cation exchanged is given by its electrostatic charge, the rate constants associated with the exchange of cations with different charges

TABLE 2. Potentiometric Measurements During the $Cu^{2+}$-$H^+$ Exchange Reaction[a]

| $t$, s | pH | $-\ln(1 - F)$[b] | $10^3\ R$, $s^{-1}$ [c] |
|---|---|---|---|
| 200 | 3.30 | 0.325 | 1.63 |
| 233 | 3.25 | 0.381 | 1.64 |
| 275 | 3.20 | 0.448 | 1.63 |
| 325 | 3.15 | 0.529 | 1.63 |
| 391 | 3.10 | 0.628 | 1.61 |
| 470 | 3.05 | 0.753 | 1.60 |
| 571 | 3.00 | 0.914 | 1.60 |
| 690 | 2.95 | 1.132 | 1.64 |
| 892 | 2.90 | 1.453 | 1.63 |

[a] [Resin] = 1.25 g/L, [$CuSO_4$] = 1.25 meq/L, temperature 25°C, stirring velocity 30 a.u.

[b] $F$ is the ratio between the proton activities at time $t$ and at the end of the reaction.

[c] Defined as $-[\ln(1 - F)]/t$.

can only be compared if the number of equivalents per liter, rather than the number of moles per liter, is the same for all the ions involved in the study. This has been taken into consideration for the experiments in Table 5.

## DISCUSSION

There are, in principle, three possible rate-controlling steps for the ion-exchange process: 1) diffusion through the film surrounding the resin particles, 2) diffusion in those particles, or 3) chemical reaction.

It is known that if diffusion inside the macromolecular particles of the resin were the rate-controlling step, the fractional attainment of equilibrium, $F$, should be proportional to the square root of time for small $F$ values [25]. Since this was not found to be the case for any of our experiments, only 1) and 3) remain.

In fact, both types of controlling mechanism lead to $-\ln(1 - F)$ being

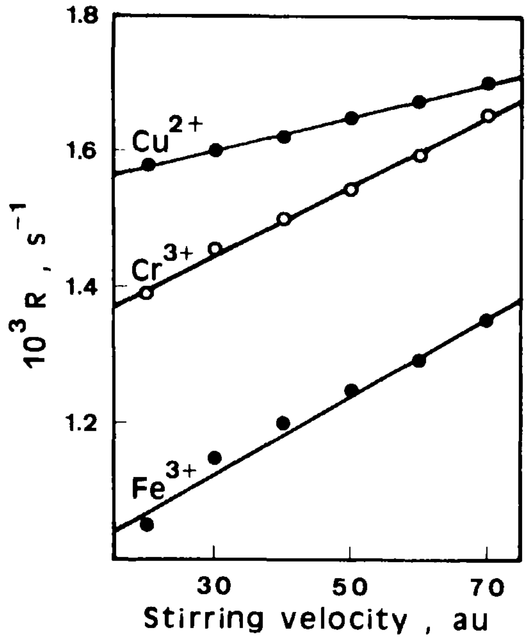

FIG. 2. Dependence of the $R$ parameter on the stirring velocity (in arbitrary units) for the $Cu^{2+}$-$H^+$ ($r = 0.998$), $Cr^{3+}$-$H^+$ ($r = 0.998$), and $Fe^{3+}$-$H^+$ ($r = 0.991$) exchange reactions. [Resin] = 1.25 g/L, [Cation] = 1.25 meq/L, temperature 25°C.

directly proportional to the time variable [25], as we found (see Table 2). Nevertheless, the dependence of the slope of those linear correlations, $R$, on the stirring velocity (see Fig. 2) permits a choice between those two possible rate-controlling steps.

If we take into account that stirring of the solution results in a decrease in the thickness of the film surrounding the resin particles, and so in an increase in the diffusion rate through that film (cf. Fig. 2), while the chemical reaction should not be affected. Thus, diffusion through the aqueous layer surrounding the macromolecular particles of resin is the actual rate-determining step for the whole process.

Therefore, the first-order dependence of the reaction rate on both the resin and the cation concentrations (see Table 1 and Fig. 1) is not chemical in its ultimate origin, but physical instead, for diffusion is the true controlling step.

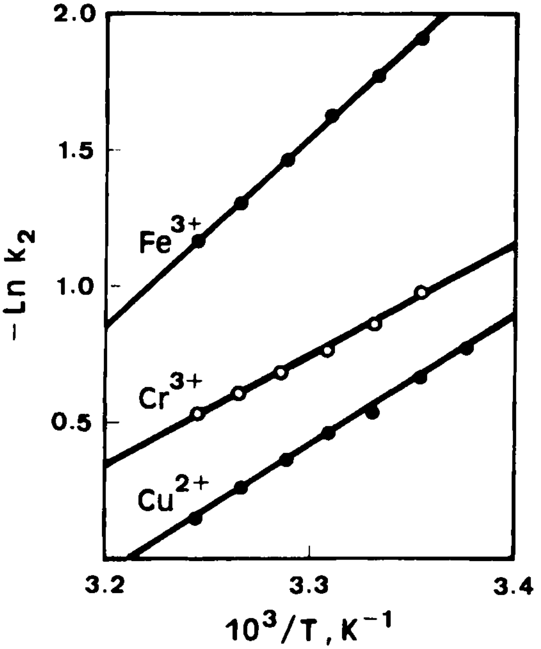

FIG. 3. Arrhenius plots for the second-order rate constant (in $M^{-1} \cdot s^{-1}$) of the $Fe^{3+}$-$H^+$ ($r = 0.999$), $Cr^{3+}$-$H^+$ ($r = 0.999$), and $Cu^{2+}$-$H^+$ ($r = 0.999$) exchange reactions. [Resin] = 1.25 g/L, [Cation] = 1.25 meq/L, stirring velocity 30 a.u.

It is well known that many linear correlations between the enthalpy and the entropy of activation found in the literature are in fact the consequence of experimental errors and must thus be discarded [27]. Nonetheless, the $\Delta H_{\ddagger}^{\circ}$ vs $\Delta S_{\ddagger}^{\circ}$ linear plot found in Fig. 4 must be accepted as genuine if the criteria proposed by Petersen and coworkers [26] is to be taken as valid.

For these authors the existence of a linear correlation between the enthalpy and the entropy of activation is likely a consequence of random errors if the total variation observed in the enthalpy of activation is less than twice the highest of the maximum possible errors associated with the enthalpies. The total variation of the activation enthalpy is 23.4 kJ/mol (the difference between those values corresponding to $Cr^{3+}$ and $Fe^{3+}$ ions in Table 3), while the highest of the maximum possible errors of the enthalpies is that

TABLE 3. Activation Parameters[a]

| Cation | $E_a$, kJ/mol | $\Delta H_{\ddagger}{}^{\circ}$, kJ/mol | $-\Delta S_{\ddagger}{}^{\circ}$, J/(K·mol)[b] |
|---|---|---|---|
| $Cr^{3+}$ | 33.7 | 31.2 | 148 |
| $Cu^{2+}$ | 39.0 | 36.5 | 128 |
| $Mg^{2+}$ | 44.9 | 42.3 | 109 |
| $Fe^{3+}$ | 57.1 | 54.6 | 78 |

[a] [Resin] = 1.25 g/L, [Cation] = 1.25 meq/L, stirring velocity 30 a.u.

[b] The activation entropies are referred to the 1 *M* standard state.

TABLE 4. Maximum Possible Errors in the Activation Parameters[a]

| Cation | $10^2 \alpha$[b] | $\delta$, kJ/mol[c] | $\sigma$, J/(K·mol)[d] |
|---|---|---|---|
| $Cr^{3+}$ | 1.2 | 1.9 | 6.4 |
| $Cu^{2+}$ | 1.8 | 2.2 | 7.6 |
| $Mg^{2+}$ | 1.1 | 1.7 | 5.8 |
| $Fe^{3+}$ | 1.7 | 2.6 | 8.7 |

[a] Temperature intervals: 25.0-35.0°C (for $Cr^{3+}$, $Mg^{2+}$, and $Fe^{3+}$) and 23.0-35.1°C (for $Cu^{2+}$).

[b] Maximum fractional error in the rate constants

[c] Maximum possible error in the activation enthalpy.

[d] Maximum possible error in the activation entropy.

of the $Fe^{3+}$-$H^+$ exchange reaction, 2.6 kJ/mol (see Table 4). Accordingly, the validity of the linear relatipnship in Fig. 4 must be accepted.

The corollary that can be extracted from the linear plot in Fig. 4 is that the exchange reactions of the different cations, at least as far as our four cases are concerned, proceed along similar lines, the rate-controlling step being the same in all the cases.

We can see in Table 5 that, for cations with the same electrostatic charge, the rate of exchange increases with the ionic radius, the $UO_2{}^{2+}$ ion being the only exception. Furthermore, for cations with identical or similar ionic radii (for instance, $Cu^{2+}$ and $Cr^{3+}$), the reaction rate decreases as the electrostatic charge increases.

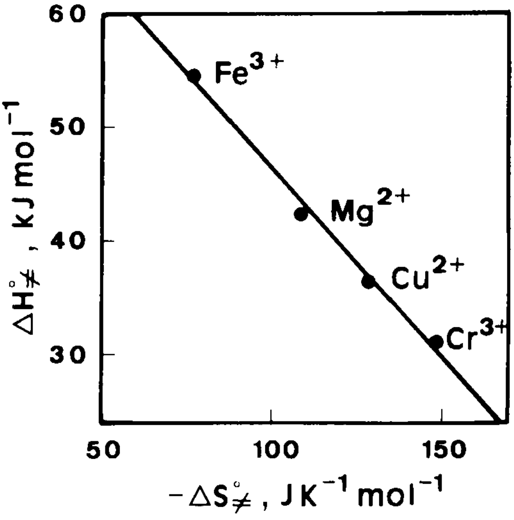

FIG. 4. $\Delta H_{\ddagger}^{\circ}$ vs $\Delta S_{\ddagger}^{\circ}$ plot for the $Fe^{3+}$-$H^+$, $Mg^{2+}$-$H^+$, $Cu^{2+}$-$H^+$, and $Cr^{3+}$-$H^+$ exchange reactions (isokinetic temperature = 333 K, $r = 0.995$). [Resin] = 1.25 g/L, [Cation] = 1.25 meq/L, stirring velocity 30 a.u.

TABLE 5. Second-Order Rate Constants for the Exchange Reaction[a]

| Cation | Ionic radius, Å[b] | $k_2$, $(M{\cdot}s)^{-1}$ |
|---|---|---|
| $Na^+$ | 0.95 | 0.98 |
| $K^+$ | 1.33 | 1.33 |
| $Mg^{2+}$ | 0.65 | 0.56 |
| $Cu^{2+}$ | 0.69 | 0.71 |
| $UO_2^{2+}$ | 7.20 | 0.45 |
| $Fe^{3+}$ | 0.64 | 0.36 |
| $Cr^{3+}$ | 0.69 | 0.49 |
| $Ce^{3+}$ | 1.11 | 0.87 |

[a] [Resin] = 1.25 g/L, [Cation] = 1.25 meq/L, temperature 25.0°C, stirring velocity 50 a.u.

[b] From typical values in the literature for the crystalline form.

All these results can be explained in terms of solvation, for the ions with small electrostatic charge and big ionic radius are less strongly solvated than those highly charged and of small radius. Since solvation results in a considerable increase in the effective ionic size, those ions with a smaller degree of hydration will diffuse faster through the aqueous layer surrounding the resin particles.

The finding that $UO_2^{2+}$ ion exchanges at a low rate despite its big size (see Table 5) may be due to the fact that this cation is so bulky it has very slow diffusion through the film surrounding the resin particles.

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