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Publisher *Taylor & Francis*

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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Mata, Fernando and Villamanaan, Rosa(1981) 'Kinetics of Potassium Ion-Exchange in a Cation-Exchange Resin', Journal of Macromolecular Science, Part A, 16: 2, 451 – 459

To link to this Article: DOI: 10.1080/00222338108058482

URL: <http://dx.doi.org/10.1080/00222338108058482>

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Kinetics of Potassium Ion-Exchange in a Cation-Exchange Resin

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ABSTRACT

The kinetics of the exchange of potassium ions in a cation-exchange resin has been studied. The rate measurements have been made by a potentiometric technique, and both the kinetic and the activation parameters of the reaction were determined. The rate-controlling step, at the beginning of the reaction, has proved to be the diffusion of the K^+ ions through the film surrounding the resin beads.

INTRODUCTION

The exchange reactions involving ions in solution and macromolecular resins are certainly interesting because of their practical importance. A number of recent reviews on this topic deal with general problems of ion exchange [1], with its physicochemical aspects [2], and also with the ion-exchange equilibrium and ion-exchange kinetics [3]. But the details of the ion-exchange reactions are far from being clear although it seems to be certain [4] that the diffusion of

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ionic species through a liquid film bounding the resin beads (film kinetics) or, alternatively, in the resin phase (gel kinetics) are the steps which determine the rate of the exchange reaction. On the other hand, Frölich's results [5] have shown that a quantitative evaluation of the ion exchange in dynamical conditions is a good procedure for deciding the rate-determining step of these reactions. Thus the quantitative study of the kinetics of the ion-exchange remains, in our opinion, one of the most adequate methods to understand its mechanism. These and similar reasons have originated some interest in a systematic investigation on the ion-exchange kinetics that has been (and still is being) carried out in our laboratory to try to clarify its mechanism. In this paper we offer the results using a macroporous resin, Lewatit-S100, which is a polystyrene-type cation exchanger. The kinetic approach requires that the substances present be in extreme dilution and this fact makes the following of the ion-exchange reaction more difficult. Fortunately, a potentiometric measurement of pH of the reaction mixture proved to be adequate.

Boyd et al. [6] have pointed out that the ion-exchange mechanism is related to the internal structure of the resin. The internal physical structure of some organic exchangers very similar to Lewatit-S100 (e.g., Lewatit-SP120) has been considered by Weatherly et al. [7] by using both a spherical model and a bidisperse structure model. On the other hand, Frölich et al. [4] have studied the ion exchange on Wofatit-KPS which is also very close to Lewatit-S100, and they proposed a new criterion for predicting the mechanism of the ion-exchange reactions. Our findings support the bidisperse structure model which was used by Weatherly et al. [7], but they are only in partial agreement with Frölich et al.'s [4] predictions. We think, however, that our findings actually improve knowledge of the behavior of Lewatit-S100, mainly in the first stage of the ion-exchange reaction, concerning both the formal aspects of the ion-exchange kinetics (kinetic orders) and the activation parameters of this reaction. In this sense, our results can be applied to any other cation exchanger with a structure similar to Lewatit-S100 (e.g., Dowex-50, Amberlite-IR120, Zerolit-225, and Lewatit-SP120). Thus our results should be of general validity, though requiring care in the application to any number to other materials.

EXPERIMENTAL SECTION

The chemicals used (KCl, HCl, and KOH) were Merck of analytical reagent quality. Lewatit-S100 was Bayer (its particle size being in the range 0.3-1.2 mm), and it was used in the H⁺-form. In the preparation of the solutions, freshly twofold distilled water was used and its specific conductivity was kept to less than 1.5 μ s/cm. The acidity of the solutions of potassium chloride was adjusted to the desired values by using very dilute solutions of HCl and KOH, the pH being controlled by potentiometric measurement. The conductivity measurements were made by a Radiometer Instrument, Model

CDM3, equipped with a conductivity cell CDC304. The control of pH was made with a Radiometer Potentiometer, Model 26 (accuracy: ± 0.005 pH units), by using a combined electrode. The temperature was kept constant within an error of $\pm 0.01^\circ\text{C}$ by a conventional thermostat, and the experiments were carried out from 20 to 30°C . A paddle stirrer was used, the stirring velocity being controlled by a rheostat calibrated in arbitrary units (au).

A 1-L beaker immersed in the thermostat acted as container for 700 cm^3 of solution in which the stirrer and the electrode or the conductivity cell were placed.

The resin was air-dried at room temperature, the dryness being controlled by weight loss. Weighted samples of dry resin were used. The number of equivalents of the ion exchanger at the beginning of the reaction was determined from the weight of the sample and the exchange capacity of the exchanger, measured in separate determinations. These determinations were made by both potentiometric and volumetric methods. The first one consisted of actually following the pH changes of a stirred resin suspension by adding known quantities of 0.1 M potassium chloride solution. These additions were made until no change of pH was detected. The final pH was taken as a measure of the active H^+ -points in the resin phase. The volumetric determination of the resin capacity was performed by adding an excess amount of potassium hydroxide solution in a resin suspension which was stirred in order to increase the rate of the exchange reaction. By separating the resin phase, a titration of the solution was made. A mass balance on OH^- species enabled us to know the concentration of the active H^+ -points in the resin. Both methods give almost the same values for the exchange capacity, 3.58 mEq/g of dry resin.

In the kinetic experiments the procedure was as follows: A known quantity of dry resin was placed in contact with a known volume of potassium chloride solution (of a known composition) which had been previously stirred and thermostated. The stirrer had to be kept at the same height above the bottom of the beaker in all experiments, as this height affects the degree of the stirring and therefore the thickness of the diffusion layer. For the same reason, the total volume of the solution was maintained at the same value (700 cm^3) in all experiments. As a result of ion exchange with the resin, the solution composition changed and this change was monitored by a combined electrode. The electrode was protected by a wire gauze to prevent the smallest particles of the resin reaching it and, consequently, disturbing the measurements. Some determinations were repeated a good number of times, using fresh portions of dry resin for each experiment, in order to check the results. Under the same experimental conditions, the agreement between the values obtained for the rate constant was satisfactory.

Numerical treatment of the experimental data was processed by a Hewlett-Packard Calculator, Model 9100.

RESULTS

Previous experiments were carried out with acidities starting at pH = 3, 6, and 10, the rest of the experimental conditions being kept constant. It was observed that changes in the concentration of the H^+ species, as a result of the ion-exchange reaction, were almost identical. This means that the acidity of the starting solution is not critical in conditioning the exchange ability of resin versus a given amount of potassium chloride. We can conclude that Lewatit-S100 is actually a strong cation exchanger under the experimental conditions used in this work. All the kinetic experiments, however, were carried out at pH = 5. Under these conditions the reaction rate is too high so that a great number of experimental points can be obtained. This is very important, mainly at the beginning of the reaction where the rate measurements were made (*vide infra*).

Measurements of the pH of the reaction mixture were made for at least half an hour. The results of a typical run are shown in Fig. 1A where the values of the proton's activity at the time t , a_{H^+} , are corrected for the pH at the beginning of the reaction. Thus a_{H^+} is the actual proton activity as originated by the ion-exchange process, the reaction rate being $v = da_{H^+}/dt$. On the other hand, it can be seen

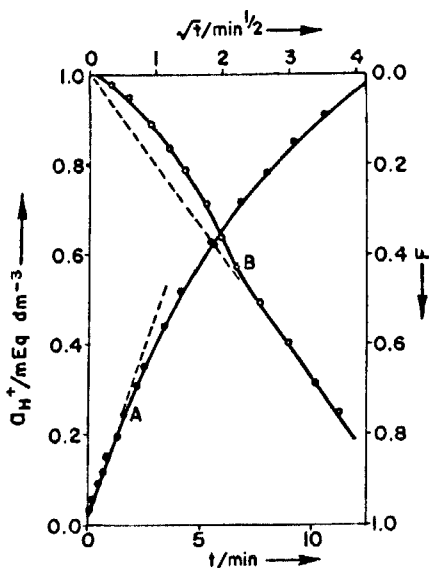


FIG. 1. Dependence of a_{H^+} (●A) and F (○B) on the time. [ClK] = 1.1×10^{-3} M; resin, 1.5 g; temperature, 25°C; SV = 20 au.

from Fig. 1A that the first experimental points fit very well into a straight line (dashed line A). Therefore the slopes of these straight lines are the experimental rates at the beginning of the reaction, v_0 . Analysis of the results has been made in a kinetic manner and, consequently, the values of v_0 were used to determine the kinetic orders of both the resin and the K^+ species in solution. The rate equation was provisionally outlined as follows:

$$v = da_{H^+}/dt = k_{\text{exp}} [RH]^{n_1} [K^+]^{n_2} \quad (1)$$

where $[RH]$ and $[K^+]_s$ are the concentrations of the active H^+ points on the resin phase and the concentration of K^+ species in solution, respectively. The results of the v_0 determinations are given in Table 1, the analysis of these findings leading to the n_1 and n_2 values which are also given in Table 1. These results mean that one can consider that $n_1 = n_2 = 1$. However, the elucidation of the rate-determining step of the reaction rate (vide infra) proves that the reaction rate has to be considered as pseudo-first-order with respect to the concentration of the active H^+ points on the resin phase. Thus a first-order kinetic equation was used to determine the experimental rate constant, k_{exp} .

The study of the temperature influence on k_{exp} (see Table 2) allow the calculation of the activation energy, E_a , and the enthalpy and the entropy of activation, ΔH^\ddagger and ΔS^\ddagger . Their values are given in Table 2.

DISCUSSION

In interpreting the kinetic orders, n_1 and n_2 , the point to point analysis of the plot of a_{H^+} vs t (min) was very useful. This analysis was carried out by calculating the fractional attainment of equilibrium which was defined as $F = a_{H^+}(t)/a_{H^+}(\infty)$. In Fig. 1B a plot of F vs $t^{1/2}$ is shown. If diffusion in and through the resin beads (gel diffusion) was the rate-controlling step, Boyd et al. [6] predicted that F had to be a linear function vs $t^{1/2}$ for F up to about 0.05. But this relation was not obtained at all. In fact, that linear function is evidenced only when $F = 0.5$, which corresponds to $t = 5$ min. For Wofatit-KPS, Frölich et al. [4] found that the rate of the ion-exchange reaction is controlled by gel diffusion. But from our findings (Fig. 1) it is evident that this situation only takes place above $t = 5$ min. On the other hand, Weatherly et al. [5] applied a bidisperse structure model to explain their findings using exchangers very similar to Lewatit-S100. But again, in this case that method could only be applicable when $t = 5$ min and more. On the contrary, a plot of $\ln(1 - F)$ vs t invariably gives

TABLE 1. Reaction Rate (v_0) and Kinetic Orders (n_1 , n_2) at the Beginning of the Reaction^a

| a) $[KCl] = 1.1 \times 10^{-3}$ M; temperature = 25°C; SV = 20 au | | |
|---|--|--------------|
| Resin (g) | $10^4 v_0 / \text{mol dm}^{-3} \text{ min}^{-1}$ | |
| 0.5 | 0.66 (0.9953) | |
| 1.0 | 1.31 (0.9999) | |
| 1.5 | 1.55 (0.9995) | $n_1 = 0.91$ |
| 2.0 | 1.83 (0.9989) | (0.9991) |
| 2.5 | 2.93 (0.9995) | |
| 3.0 | 3.32 (0.9984) | |
| b) Resin: 1.5 g; temperature = 25°C; SV = 20 au | | |
| $10^3 [KCl] / M$ | $10^4 v_0 / \text{mol dm}^{-3} \text{ min}^{-1}$ | |
| 0.22 | 0.29 (0.9982) | |
| 0.66 | 0.84 (0.9998) | |
| 0.88 | 1.30 (0.9952) | |
| 1.10 | 1.44 (0.9995) | $n_2 = 0.91$ |
| 1.54 | 2.01 (0.9975) | (0.9886) |
| 1.76 | 2.12 (0.9963) | |
| 1.98 | 2.47 (0.9994) | |
| 2.20 | 2.74 (0.9979) | |

^aThe figures in parenthesis are the linear correlation coefficients, r_{xy} .

a straight line within the range from $t = 0$ to $t = 5$ min, and the slope of this plot is actually the pseudo-first-order rate constant at the beginning of the reaction. The latter is termed [6] R or S, depending on whether the rate-determining step was the diffusion of the ionic species through a liquid film bounding the resin beads (film diffusion) or was alternatively the adsorption of these species on the resin phase.

We still have to explain the connection between these findings and the values found for n_1 and n_2 . The plot of $\ln(1 - F)$ vs t actually means that the kinetic order to the resin is $n_1 = 1$, this result supporting the determination of n_1 by using an initial rate method. The elucidation of the $n_2 = 1$ value is far from being clear, however.

TABLE 2. Dependence of k_{exp} on the Temperature: Activation Parameters of the Reaction^a (Conditions: $[\text{KCl}] = 1.1 \times 10^{-3} \text{ M}$; resin = 1.5 g; SV = 20 au)

| Temperature ($^{\circ}\text{C}$) | $10^3 k_{\text{exp}}/\text{s}^{-1}$ |
|------------------------------------|-------------------------------------|
| 20 | 2.72 (0.9985) |
| 22 | 2.75 (0.9998) |
| 24 | 3.03 (0.9990) |
| 26 | 3.38 (0.9996) |
| 28 | 3.67 (0.9990) |
| 30 | 4.00 (0.9987) |

^a $E_a = 29.4 \text{ kJ mol}^{-1}$ (0.977); $\Delta H^{\ddagger} = 33.2 \text{ kJ mol}^{-1}$ (0.998); $\Delta S^{\ddagger} = -36.6 \text{ eu}$ (0.998). The figures in parenthesis are the linear correlation coefficients, r_{xy} .

First of all, it is necessary to decide which is the rate-determining step of the whole ion-exchange reaction. In this way the study of the variation of the pseudo-first-order rate constant with the stirring velocity (SV) was conclusive (see Fig. 2). In analyzing this result a few considerations are necessary. The R parameter has been defined [6] by $R = 3D/(r_0 \Delta r_0 K)$, where D is the diffusion coefficient of the K^+ species in this case, and r_0 and Δr_0 are the radius of the resin particle and the thickness of the film surrounding it, respectively. The parameter K is the distribution efficiency which we have defined as the quotient between the concentration of the K^+ species on the resin phase, $[\text{K}^+]_{\text{RH}}$, and its concentration in the liquid phase (solution), $[\text{K}^+]_{\text{S}}$. The magnitude of the parameter K was assumed to be independent of concentration. This assumption will, of course, apply exactly only to solutions infinitely diluted in the species being adsorbed. But, in order for K to be constant, it is sufficient [6] that the adsorbate be a microcomponent of the system. Moreover, D is a constant and r_0 has to be an average value because there is a statistical distribution of the particle sizes in the range from $r_0 = 0.3$ to 1.2 mm (15-20 mesh). Thus the only variable conditioning the magnitude of the R parameter is the thickness of the film surrounding the resin particles, Δr_0 . This thickness should be an inverse function of the flow velocity and, consequently, of the stirring velocity, SV. Hence, R should increase directly with SV, and this was found in practice (see Fig. 2). If the exchange was controlled by the adsorption process, the pseudo-first-order rate constant (termed S in this case) does not change with SV. So one can conclude that the rate is

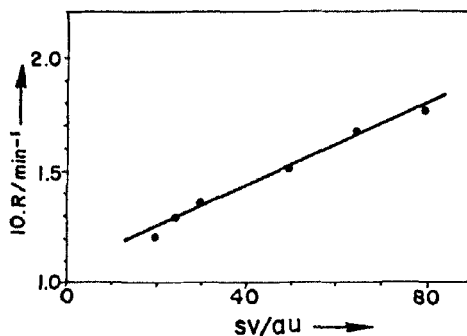
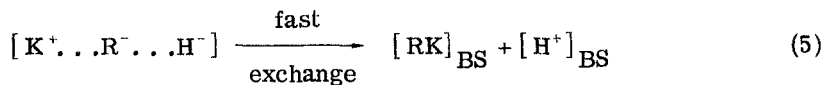
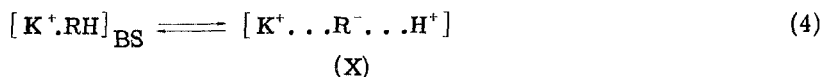
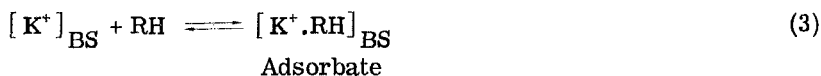


FIG. 2. Dependence of R on the stirring velocity. $[ClK] = 1.1 \times 10^{-3} M$; resin, 1.5 g; temperature, $25^\circ C$.

film-diffusion controlled. Hence, from $R = 3D/(r_0 \Delta r_0 K)$ together with the definition of the K parameter, it is clear that the "kinetic order" n_2 , with respect to the K^+ species, has to be +1, as was found.

Consequently, a reaction scheme has been stated as follows:



where s = bulk solution
 BS = bead surface
 RH = resin phase
 X = activated complex

This formulation is consistent with the idea we advanced above that the adsorbate species was a microcomponent of the system (vide supra). Moreover, the negative value found for the activation entropy also supports this assumption.

The magnitude of the activation energy is higher than the one that was found [6] when the adsorption process controls the whole reaction. But its value is only slightly larger than would be expected if the diffusion process was into the resin bead instead of through a film bounding it. If a uniform dispersion of microspheres within a macrosphere (or bead) is assumed [7], the diffusion into the resin particles and through the film surrounding it would take place in the microspheres (through the micropores) and in the macrospheres (through the macropores), respectively. This model is very useful for understanding that at the beginning of the reaction the controlling step is diffusion through the macropores because the concentration of the $[K^+.RH]_{BS}$ species should be so small that the diffusion through the micropores must be very fast. But, over $t = 5$ min, this last process should give a concentration at the microspheres surface large enough so that the diffusion through the micropores becomes difficult, this process being the rate-controlling step.

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Accepted by editor February 12, 1980

Received for publication March 5, 1980