

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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

Kinetics of Exchange of Chloride Ions in an Anion-Exchange Resin

F. Mata^a; V. Avariento^a

^a Departamento de Química física Facultad de Ciencias, Universidad de Valladolid, Valladolid, Spain

To cite this Article Mata, F. and Avariento, V.(1981) 'Kinetics of Exchange of Chloride Ions in an Anion-Exchange Resin', *Journal of Macromolecular Science, Part A*, 16: 7, 1225 – 1232

To link to this Article: DOI: 10.1080/00222338108063229

URL: <http://dx.doi.org/10.1080/00222338108063229>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Kinetics of Exchange of Chloride Ions in an Anion-Exchange Resin

FERNANDO MATA* and VICENTE AVARIENTO

Departamento de Química física
Facultad de Ciencias
Universidad de Valladolid
Valladolid, Spain

ABSTRACT

The kinetics of the exchange of chloride ions in an anion-exchange resin has been studied. The rate measurements were carried out by a potentiometric technique, and thus both the kinetic and the activation parameters of the reaction were determined. The results concerning the influence of the stirring velocity upon the fractional attainment of equilibrium prove that the diffusion of the Cl^- species into the resin beads plays an important role in the mechanism of the exchange reaction, although the exchange rate is chemical in its ultimate mechanism.

INTRODUCTION

Exchange reactions involving anions and macromolecular resins have been studied in a number of papers [1-4] which deal with the thermochemistry, the exchange equilibrium, and some other thermodynamic aspects of these reactions, but the kinetics of the anion-exchange reactions has not been considered in detail. A quantitative study of the kinetics of any reaction, however, remains the most

*To whom correspondence should be addressed.

adequate method for understanding its mechanism. For this reason we began a systematic investigation of the ion-exchange kinetics in our laboratory, the first results of which can be found in a previous paper [5].

Anion-exchange reactions differ from those of cation-exchange in a number of important aspects [6, 7]. It therefore seems convenient to begin with two parallel investigations of cation-exchange and anion-exchange reactions. In this paper we present the results of the kinetics of the chloride ion exchange with the hydroxyl anion by using a macroporous resin, Lewatit-M500, which is a polystyrene anion-exchanger. Results relating to the K^+/H^+ exchange were reported previously [5].

The results given in this paper confirm, and also improve in some aspects, the formulation of the reaction scheme that we proposed [5] for these ionic-exchange reactions, so we feel that it is of general validity when explaining the ion-exchange on macroporous resin whose internal structure was similar to Lewatit-S100 and Lewatit-M500.

EXPERIMENTAL

The chemicals used (KCl, and HCl, and KOH) were Merck of analytical reagent quality. The Lewatit-M500 was Bayer (15-50 mesh) and it was used in the OH^- form. In the preparation of the solutions, freshly twofold distilled water was used and its specific conductivity was kept to less than $1.5 \mu S/cm$. The acidity of the solutions of potassium chloride was regulated to the desired values by using very dilute solutions of HCl or KOH, the pH being recorded by a potentiometric technique.

The conductivity measurements were taken with a Radiometer instrument model CDM3 equipped with a conductivity cell CDC304. The recording of pH was made by a Radiometer potentiometer model 26 (accuracy: ± 0.005 pH units) by using a combined electrode. Temperature was kept constant within $\pm 0.01^\circ C$ by a conventional thermostat, and experiments were carried out within the range from 20 to $30^\circ C$. 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 the container for the 700 cm^3 of solution in which the stirrer, the pH electrode, or the conductivity cell were placed.

The resin was prepared and analyzed in a manner similar to the one previously described [5] for Lewatit-S100. The exchange capacity of Lewatit-M500 was 1.33 meq/g of dry resin.

The experimental procedure used in the kinetic runs has been reported in another paper [5], and the numerical treatment of the experimental data was also made, in this case, by a Hewlett-Packard calculator model 9100.

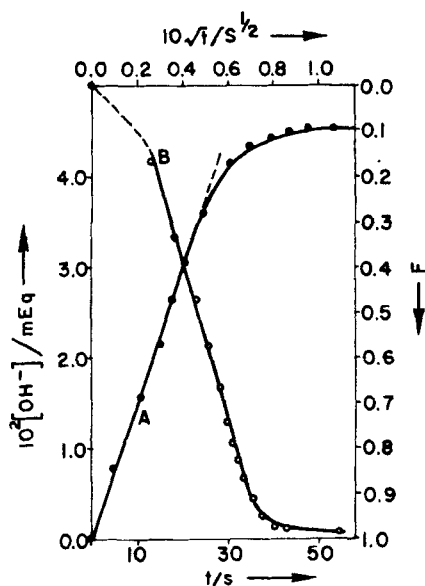


FIG. 1. Dependence of $[\text{OH}^-]$ (●A) and F (○B) on time. $[\text{ClK}] = 2.9 \times 10^{-3} \text{ M}$ (●A) and $1.5 \times 10^{-3} \text{ M}$ (○B). Resin, 1 g; temperature, 25°C ; $\text{SV} = 20 \text{ au}$.

RESULTS

The exchange reaction of the hydroxyl groups with the Cl^- ions results in an increase in the concentration of the OH^- ions $[\text{OH}^-]$ in the bulk solution, as can be deduced from the pH changes. The reaction rate was therefore followed by pH measurements and from this we could calculate the concentration of the OH^- species.

A number of experiments were carried out in order to study the exchange behavior of Lewatit-M500 with acidities beginning at $\text{pH} = 3, 6$ and 10 , the rest of the experimental conditions being kept constant. It was observed that the changes in the concentration of OH^- species, as a result of the ion-exchange reaction, were quite different. This means that the acidity of the solution at the beginning of the experiments is crucial since it conditions the exchange ability of resin versus a given amount of potassium chloride. We can conclude that Lewatit-M500 is actually a weak anion exchanger under the experimental conditions used in this work. For this reason, the exchange reaction at the resin surface is at its most efficient within the acid region of the pH scale. In this way, all the kinetic experiments were carried out at $\text{pH} = 4.5$ because, under these conditions, the reaction

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

(a) $[ClK] = 1.46 \times 10^{-3} M$; temperature = 25°C; SV = 20 au		
Resin (g)	$10^7 v_0$ (mol/dm ³ /s)	
0.75	6.75 (0.9996)	
1.00	7.33 (0.9973)	
1.25	9.86 (0.9996)	$n_1 = 0.92$
1.50	11.34 (0.9989)	(0.9823)
1.75	13.60 (0.9965)	
2.00	16.08 (0.9991)	
(b) Resin = 1 g; temperature = 25°C; SV = 20 au		
$10^3 [ClK]$ (M)	$10^7 v_0$ (mol/dm ³ /s)	
1.12	5.63 (0.9999)	
1.47	7.25 (0.9998)	
1.82	9.23 (0.9998)	$n_2 = 1.05$
2.18	10.56 (0.9996)	(0.9852)
2.52	11.85 (0.9910)	
2.88	16.48 (0.9937)	

^aThe figures in parenthesis are the linear correlation coefficients.

rate is not too high, and therefore a great number of experimental points can be obtained at the beginning of the reaction, where the rate measurements were made (*vide infra*).

The pH measurements of the reaction mixture (corrected for the pH at the beginning of the reaction) were made for at least half an hour. The results of a typical run are shown in Fig. 1 (Curve A) where $[OH^-]$ is the actual concentration of the hydroxyl ions as originated by the ion-exchange process.

The reaction rate has been defined as $v = d/dt [OH^-]$, and the rate equation was provisionally outlined as

$$v = \frac{d[OH^-]}{dt} = k_{\text{exp}} [ROH]^{n_1} [Cl^-]^{n_2} \quad (1)$$

where $[ROH]$ and $[Cl^-]$ are the concentrations of the active hydroxyl points in the resin phase and the concentration of the Cl^- species in solution, respectively. From the reaction rate at the beginning of the reaction, v_0 , the kinetic orders, n_1 and n_2 , were determined in a

TABLE 2. Dependence of k_{exp} on the Temperature: Activation Parameters of the Reaction^a

Temperature (°C)	$10^{-3}k_{\text{exp}}$ (mol ⁻¹ dm ³ /s)
20	1.18 (0.9999)
22	1.33 (0.9998)
24	1.51 (0.9991)
26	1.81 (0.9999)
28	2.09 (0.9999)
30	2.41 (0.9994)
$E_a = 53.0 \text{ kJ/mol (0.9964); } \Delta H^\ddagger = 50.5 \text{ kJ/mol} \left. \vphantom{\begin{matrix} E_a \\ \Delta S^\ddagger \end{matrix}} \right\} (0.9960)$ $\Delta S^\ddagger = -19.5 \text{ eu}$	

^aThe figures in parenthesis are the linear correlation coefficients. Conditions: [ClK] = 1.46×10^{-3} M; resin = 1g; SV = 20 au.

similar way as previously described [5]. Their values (see Table 1) allow us to consider that $n_1 = n_2 = 1$. This fact, together with our findings concerning the nature of the rate-determining step (vide infra), permits one the use of a second-order kinetic equation to determine the experimental rate constant, k_{exp} .

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

DISCUSSION

As for the K^+/H^+ system, analysis of our findings was made by using the fractional attainment of equilibrium, F . For this system it was defined as $F = [\text{OH}^-]_t / [\text{OH}^-]_\infty$. If diffusion into and through the resin beads is the rate-determining step for the whole reaction, Boyd et al. [8] predicted that F had to be a linear function of $t^{\frac{1}{2}}$ (t being the time) for F up to about 0.05. In Fig. 1 (Curve B), one of the plots of F vs $t^{\frac{1}{2}}$ is shown. From any of these plots it is clear that Boyd's relation is not fulfilled. In this work the values of F range from 0.2 to 0.9 which are outside the interval given for this parameter as formulated by Boyd et al.'s [8] model, but it is not for this reason that the Boyd model is not applicable [5]. If now the model is not valid (see Fig. 1, Curve B), it is because diffusion into and through

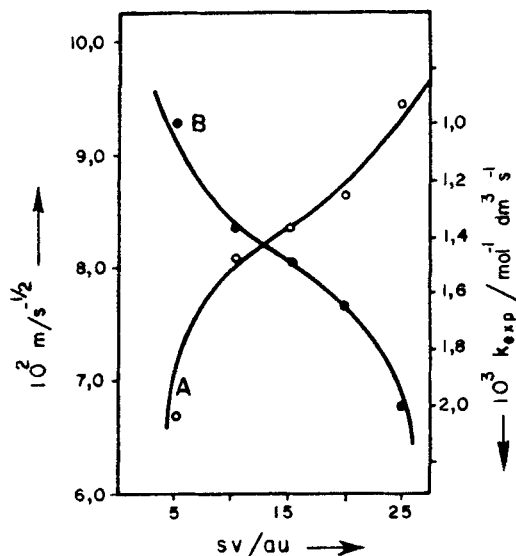


FIG. 2. Dependence of m (○ A) and k_{exp} (● B) on the stirring velocity, SV. $[ClK] = 1.5 \times 10^{-3} M$; resin, 1 g; temperature, 25°C.

the resin beads are not the steps determining the exchange rate. Hence, in the present case, both n_1 and n_2 are true kinetic orders while for the K^+/H^+ system [5] the order n_2 with respect to the ion which is exchanged on the resin surface is only an apparent one which appears in the rate equation as a result of film diffusion.

For all the above reasons a second-order rate equation was used to calculate the k_{exp} values (vide supra). This fact also explains why the magnitude of the activation parameters is quite different for this system compared to the K^+/H^+ system. The activation energy is now doubled. Besides, the entropy of activation is -19.5 vs -36.6 eu for that exchange reaction. An enhancement of the activation entropy is consistent with the formation of "water structure enforced ion pairs" [9-11] between large tetraalkylammonium groups on the resin surface and large anions (e.g., chloride ions) in solution. All these facts mean that the exchange rate is chemical in its ultimate mechanism, so that the exchange on the resin surface of the Cl^- ions by the hydroxyl groups (chemical step in the mechanism [5]) has to be at least as slow as the diffusion of the Cl^- species.

The plot of F vs $t^{1/2}$ (Fig. 1 Curve B) clearly shows, however, that there exists a very wide range (almost 50% of each run) where F is a linear function of $t^{1/2}$, so that diffusion into and through the resin beads

plays an important role in the mechanism. The slope of that linear region has been termed m , and Fig. 2 (Curve A) shows, for a typical case, that m increases when the stirring velocity, SV , is increased. This fact is not in agreement with the predictions of Boyd et al. [8] for diffusion into the resin because, in this case, a nondependence of m on SV should have been found. On the other hand, if the whole exchange reaction was chemically rate-controlled, the rate constant, k_{exp} , should be independent of particle diameter and the stirring velocity, and it would depend only on the rest of the experimental conditions. In Fig. 2 (Curve B), one of the plots of k_{exp} vs SV is given which shows that k_{exp} actually depends on SV . Moreover, Fig. 2 (Curves A and B) seems to have almost the same profile, so the origin of the dependence of both m and k_{exp} upon SV appears to be common.

From this situation we should have to conclude that, as we have already stated, the chemical exchange is not clearly rate-determining against the diffusion step, so that these two steps have to be of comparable slowness. Moreover, that diffusion is actually (vide supra) gel diffusion (diffusion into the resin beads), but it has to take place through a region with an average thickness of Δr_0 . Thus, from Boyd et al.'s reasoning [8], it is very easy to show that $m = 6/\Delta r_0 (D_1 \pi)^{1/2}$, D_1 being the internal diffusion coefficient of the Cl^- species. The value of Δr_0 is actually the thickness of the micropores between the microspheres within the beads or macrospheres [5, 12], and its value has to be conditioned by the stirring velocity, SV . This explains our findings in Fig. 2 (Curve A).

Therefore, the findings concerning Lewatit-M500 confirm the reaction scheme that we have already proposed [5] for the ion-exchange reactions although a number of refinements have been made in this case. It will be necessary, however, to obtain more experimental data so as to confirm if all these ideas are of general application for ionic exchange reactions on macroporous resins.

REFERENCES

- [1] G. R. Choppin, G. Y. Markovits, and M. E. Clark, J. Phys. Chem., **76**, 680 (1972).
- [2] F. Vaslow and G. E. Boyd, Ibid., **70**, 2507 (1966).
- [3] R. J. Irving, M. H. Abraham, J. E. Salmon, A. Marton, and J. Inczedy, J. Inorg. Nucl. Chem., **39**, 1433 (1977).
- [4] S. Lindenbaum, L. Leifer, G. E. Boyd, and J. W. Chase, J. Phys. Chem., **74**, 761 (1970).
- [5] F. Mata and R. Villamañan, J. Macromol. Sci.-Chem., **A16**, 451 (1981).
- [6] G. E. Boyd, S. Lindenbaum, and G. E. Myers, J. Phys. Chem., **65**, 577 (1961).

- [7] H. P. Gregor, J. Belle, and R. A. Marcus, J. Am. Chem. Soc., 77, 2713 (1955).
- [8] G. E. Boyd, A. W. Adamson, and L. S. Myers, Ibid., 69, 2836 (1947).
- [9] S. Lindenbaum and G. E. Boyd, J. Phys. Chem., 68, 911 (1964).
- [10] H. S. Frank, Z. Phys. Chem., 228, 367 (1965).
- [11] R. M. Diamond, J. Phys. Chem., 67, 2513 (1963).
- [12] L. R. Weatherly and J. C. R. Turner, Trans. Inst. Chem. Eng., 54, 89 (1976).

Accepted by editor June 24, 1980

Received for publication October 4, 1980