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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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Athanasios G. Theodoropoulos<sup>a</sup>; Demetrios L. Bouranis<sup>b</sup>; Apostolos G. Vlyssides<sup>a</sup>; Elisabet D. Kotsibou<sup>a</sup>

<sup>a</sup> Laboratory of Organic Chemical Technology, Department of Chemical Engineering, National Technical University of Athens, Athens, Zografou <sup>b</sup> Laboratory of Plant Physiology, Department of Agricultural Biology and Biotechnology, Agricultural University of Athens, Athens, Greece

**To cite this Article** Theodoropoulos, Athanasios G. , Bouranis, Demetrios L. , Vlyssides, Apostolos G. and Kotsibou, Elisabet D.(1996) 'Ion-Exchange Kinetics in Highly Swellable Macronets', Journal of Macromolecular Science, Part A, 33: 1, 281 – 288

**To link to this Article:** DOI: 10.1080/10601329608020384

**URL:** <http://dx.doi.org/10.1080/10601329608020384>

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## ION-EXCHANGE KINETICS IN HIGHLY SWELLABLE MACRONETS

Athanasios G. Theodoropoulos<sup>1</sup>, Demetrios L. Bouranis<sup>2</sup>,  
Apostolos G. Vlyssides<sup>1</sup>, and Elisabet D. Kotsibou<sup>1</sup>

1. Laboratory of Organic Chemical Technology, Department of Chemical Engineering, National Technical University of Athens, 157 73 Zografou, Athens, Greece.
2. Laboratory of Plant Physiology, Department of Agricultural Biology and Biotechnology, Agricultural University of Athens, 118 55 Athens, Greece.

### ABSTRACT

*Mathematical models were tested in order to describe the kinetics of ion-exchange in highly swellable macronets. Ion-exchange was found to proceed rapidly compared to swelling kinetics. From the typical differential rate equations that were applied and integrated, it was shown that second order kinetics represent the describing system, in respect to the remaining ion-exchange sites.*

### INTRODUCTION

Ion-exchange processes in macronet ionic networks are of importance, as derived from the wide possible application in both industrial and laboratory level. The availability of ion-exchange sites combined with the high swelling ability is promising for soil-conditioning, diappers technology, ion and solvent separation, i.e. in areas where swellable polymers of uniform structure are required<sup>(1-3)</sup>.

Although the swelling behaviour of macronet is well studied<sup>(4,5)</sup>, a lack of detailed information exist, concerning their ion-exchange properties. The general aspects of the kinetic behaviour of ion-exchangers is understood for simple systems. However, in the case of macronets due to their high swelling ability the boundary conditions are more complex than in standard ion-exchangers.

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\*Corresponding author

The group of Boyd have indicated that ion-exchange kinetics is primarily based on transport phenomena<sup>(7,8,9)</sup>. According to their theory, the rate controlling step was suggested to be diffusion: (i) in the external solution up to the surface of the polymer (film diffusion), and (ii) in the polymer particle itself (particle diffusion).

An intermediate range of both mechanisms may also exist while the chemical exchange in the vicinity of the exchange groups is in general extremely rapid to be taken into consideration. In such phenomena, rate equations based on physical theoretical background and mechanistic approaches known to occur provide analytical information.

In fact diffusion coefficient is difficult to be calculated without assumption in ion-exchangers for several reasons<sup>(9-13)</sup>. First, a part of the cross section area in the polymer is occupied by the network chains and is not available for ion-penetration. Second, large ions may be impeded in the mobility by the network. Third, the interaction of the charged ions with the fixed ionic groups have to be taken into account. Fourth, concerning penetration from glassy state, the diffusion paths can be changing during ion-exchange process. The last reason is more important for highly swellable polymers like macronets.

Since the need for a descriptive model in the various fields of application of macronets still remains, in the present correspondence we attempt to fit some typical mathematic equations on experimental data.

## MATERIALS AND METHODS

Three crosslinked sulfonated polystyrene macronets were tested in respect to ion-exchange kinetics. The first two samples were prepared according to a "one-pot" suspension technique<sup>(14)</sup> having 4% w/w crosslinking agent concentration and ion-exchange capacity 4.85 meq/g. Two particle size fractions were selected having particle size range in dry form within 0.32-0.40 mm (Sample A) and 0.40-0.63 mm (Sample B) respectively.

Since the above described polymer were prepared according to a suspension technique and the achieved particles remained in a rather narrow range, a third sample of macronet sulfonated polystyrene was prepared via a two-step solution technique, by using conc.  $H_2SO_4$  as sulfonating medium. Following crosslinking according to a solution technique<sup>(15)</sup>, the networks was purified, dried and crushed in a hammermill. The fractions selected for further treatment were between 1.60-3.15 mm (sample C). The nominal crosslinking agent concentration was 4% w/w. However, sulfonation was extended to 6 hrs, due to the penetration requirements of the sulfonating medium. The ion-exchange capacity of the obtained products was 3.91 meq/g.

Following preparation all samples were extensively purified using methanol and distilled water and the acidic form of the ionic groups was ensured by remaining in a 1N HCl solution for 24 hours and consequently washings with a 0.01N HCl

solution. The networks were finally dried at 105 °C until constant weight was achieved.

Ion-exchange kinetics was followed according to a batch method. All samples (0.1–0.2 g) in the acidic form were introduced to an Erlenmeyer flask and 40 ml of a standard 0.5N NaCl solution were added at 25±1 °C. The ion-exchange process was terminated at the appropriate time by immediate filtration under vacuum and subsequent washing with 5x5 ml of redistilled water. The total filtrate was titrated against a standard alkaline solution for hydrogen ions.

## RESULTS AND DISCUSSION

Figure 1 illustrates the ion-exchange kinetics curves at 25 °C and figure 2 the percentage fraction ( $\alpha$ ) of ion-exchange sites occupied by Na<sup>+</sup> ions as a function of ln(time). The ion-exchange results are expressed as meq of sodium per gram of dry polymer coming from the following obvious equations:

$$i = V_{\text{alc}} \times N_{\text{alc}} / mp \quad (1)$$

and

$$\alpha = i/i_{\infty} \times 100 \quad (2)$$

where:  $V_{\text{alc}}$ : is the volume (ml) of the alkaline solution

$N_{\text{alc}}$ : is the normality of the same solution

$mp$ : are the groups of the dry polymer in the acidic form

$i$ : are the meq/g of polymer occupied by Na<sup>+</sup> ions at the present time, and

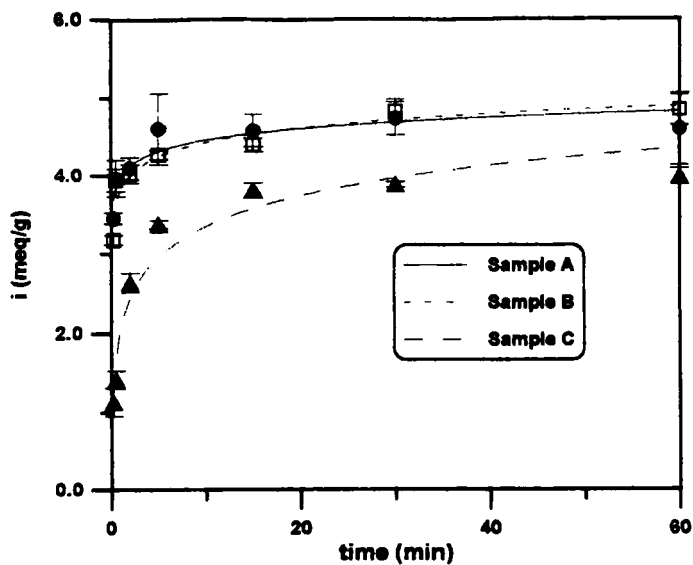
$i_{\infty}$ : is the ion-exchange capacity of the polymer in equilibrium conditions.

According to figures 1 and 2, similar results are obtained for samples A and B that have similar particle size range, while in the case of sample C, ion-exchange proceeds slower, due to the larger average particle size. A comparison of the observed curves with analogous curves indicating swelling kinetics having particle sizes in the same order of magnitude<sup>(5)</sup>, indicates that swelling proceeds with slower rates in respect to ion-exchange.

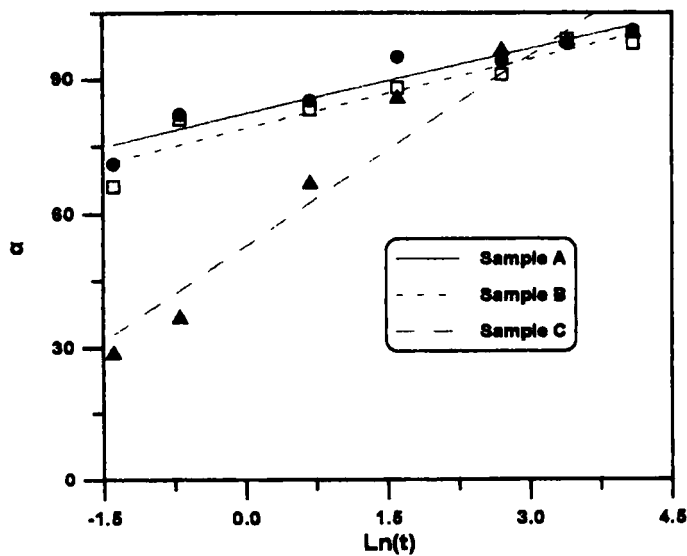
During the following analysis the system will be assumed as isothermic and the particles uniform and of equal size. As discussed in the introductory section, the high swelling ratios of the studied macronets make difficult to apply the Nernst-Planck and Fick diffusion equations. However, a model adequate to predict the ion-exchange behaviour of macronets is necessary for applications. Thus some typical differential rate equations were tested and integrated in order to describe the studied system.

This section examines the possibility that ion-exchange follows zero-order kinetics. According to zero-order kinetics the rate of ion-exchange at any given time ( $t$ ) is constant. If  $k$  is the proportionality constant then:

$$di / dt = k \quad (3)$$



**FIGURE 1.** Ion exchange capacity for the exchange  $H^+ \rightarrow Na^+$  as a function of time at 25 °C.



**FIGURE 2.** The percentage fraction of ion-exchange sites occupied by  $Na^+$  ions as a function of  $\ln(t)$  at 25 °C.

which integrates to:

$$i = kt + C \quad (4)$$

where C is constant. Figure 1 represents also zero-order kinetics. The correlation coefficients are  $r_A=0.75$ ,  $r_B = 0.74$  and  $r_C=0.70$  respectively, while the theoretical correlation coefficient for 99% confidence limits and 7-2=5 degrees of freedom is  $r_{th}=0.87$ . Thus, the correlation is not statistically significant.

According to first-order kinetics the rate of ion-exchange is directly proportional to the ion-exchange that has yet to occur before the maximum or equilibrium ion-exchange ( $i_\infty$ ) has been reached:

$$di / dt = k(i_\infty - i) \quad (5)$$

which integrates to

$$\ln[i_\infty/(i_\infty-i)] = kt \quad (6)$$

Figure 3 represents fitting of the experimental data to a first-order kinetic model. The correlation coefficients in this case are:  $r_A=0.91$ , (here correspond 6-2=4 degrees of freedom and a  $r_{th}=0.92$ ),  $r_B=0.80$  (5 degrees of freedom and a  $r_{th}=0.87$ ) and  $r_C=0.80$  (4 degrees of freedom and a  $r_{th}=0.92$ ) respectively, which lead to a non-statistically significant correlation as well. The second-order equation for ion-exchange is:

$$di / dt = k(i_\infty-i)^2 \quad (7)$$

Integration between the limits  $i=0$  when  $t=0$  and  $i_\infty$  results in:

$$i = k i_\infty^2 t / (1+k i_\infty t) \quad (8)$$

Algebraic manipulation of equation (8) results in:

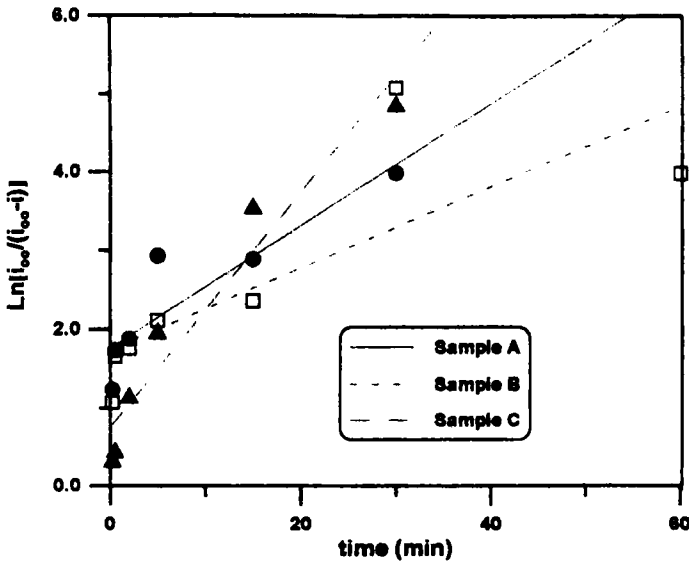
$$\begin{aligned} i &= t / (1/k i_\infty^2 + t/i_\infty) \Leftrightarrow \\ i &= t / (A + t/i_\infty) \Leftrightarrow \\ t/i &= A + (1/i_\infty) t \end{aligned} \quad (9)$$

where:  $A = 1/k i_\infty^2$  (10)

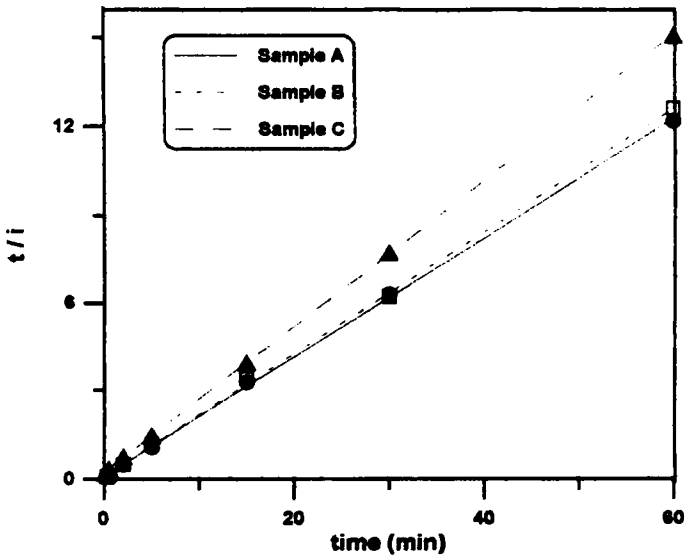
and  $k = 1/A i_\infty^2$  (11)

Figure 4 represents fitting of the experimental data to a second-order kinetic model. The correlation coefficients exceeded  $r=0.99$  in every sample series, which lead to a statistically significant correlation ( $r_{th}=0.87$  for 99% confidence limits and 5 degrees of freedom).

Table 1 presents experimental ( $i_{\infty,exp}$ ) and predicted ( $i_{\infty,pred}$ ) values of equilibrium ion-exchange capacity as derived from the second-order kinetic model, by calculating the quantity A. From the data of Table 1 we may see that experimental and predicted equilibrium ion-exchange capacity of macronets are in good agreement.



**FIGURE 3.** Fitting of ion-exchange curves to a first-order kinetic model.



**FIGURE 4.** Fitting of ion-exchange curves to a second-order kinetic model.

**TABLE 1.** Experimental and predicted values of maximum ion-exchange capacity according to the second-order kinetic model.

Sample	$i_{c,exp}$	$i_{c,pred}$
A	4.85	4.93
B	4.85	4.81
C	3.91	4.03

Substituting eq.11 into eq.7 results in:

$$di/dt = (1/A) [(i_{\infty}-i)/i]^2 \quad (12)$$

As  $t \rightarrow 0$  and  $i \rightarrow 0$ , then:

$$\lim_{t \rightarrow 0} (di/dt) = 1/A \quad (13)$$

In eq.13, A is the reciprocal of the initial ion-exchange rate corresponding to the stage where sodium ions permit to the thin film that covers polymer particles.

In conclusion, the second-order kinetic model appears to be adequate for macronet's ion-exchange kinetic description.

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