

## The Rate Determining Step in Low Capacity Surface-Type Anion Exchangers

SALEH O. BAHAFI

*Department of Chemistry, Faculty of Science,  
King Abdulaziz University, Jeddah, Saudi Arabia*

**ABSTRACT.** Study of ion exchange kinetics can give some insight into the rate controlling step and mechanism in ion exchange. In the majority of cases, diffusion of ions, either through the resin bead or through the surrounding static layer of solution is the controlling step in the exchange process.

In the rate studies to be described, a modification of the Shallow bed technique was used; chloride ions were labelled with chlorine-36 and the resin completely converted to the chloride form. After passing  $1 \times 10^{-5}$  M HCl through the bed for the appropriate time at constant flow rate, the chloride was displaced completely from the resin by nitrate. The chloride solution was monitored using a suitable scintillation cocktail which measured the chlorine-36.

Results from a study of several ion-exchangers, including Dionex resins will be presented and discussed.

### Introduction

Low capacity anion exchangers are the most widely used stationary phase in ion chromatography; typical capacity lies in the range of 0.01-0.1 mequiv./g. The rate at which ion exchange between a resin and the external (mobile) phase can be important in determining the efficiency of ion chromatography columns<sup>[1]</sup>. Hellferich<sup>[2]</sup> has summarized the early work on ion exchange kinetics. In the majority of cases the rate of ion exchange is controlled by diffusion of ions either through the resin bead or through the surrounding static solution (the Nernst film). Boyd and co-workers<sup>[3]</sup> divided the exchange process of ion between a resin particle and the solution into five steps. Where A is an ion in solution, exchanging with B in the resin, the steps are:

- 1) Diffusion of A through the solution to the resin particle;
- 2) Diffusion of A through the resin particle;
- 3) Exchange between A and B at the exchange sites;

- 4) Diffusion of B through the resin into the resin-solution interface; and
- 5) Diffusion of B through the solution, away from the resin.

Step 3, could involve chemical reaction as might occur for example in chelating resins, but has never been proved conclusively<sup>[4-8]</sup>, steps 1 and 5 may be reduced to negligible effect by sufficiently rapid agitation of the solution. Thus, the two best defined rate determining step are<sup>[2,3,8]</sup>

- 1) Particle diffusion
- 2) Film diffusion

Most commonly, however, neither one of these steps is rate controlling, and both may be considered to contribute.

Isotope exchange gives rise to the simplest kinetic situation. For a reaction that is controlled by diffusion within the particle, the fractional attainment of equilibrium,  $F$ , as a function of time,  $t$ , is given by

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \cdot \exp \left[ -\frac{Dt^2 n^2}{r^2} \right]$$

where  $r$  is the radius of the particle,  $D$  is the inter diffusion coefficient of the resin and  $n$  represents the integers from 1 to  $\infty$ ,

By substituting  $F = 0.5$ , the half time of exchange may be calculated from equation

$$t_{1/2} = \frac{0.030 r^2}{D}$$

### Liquid Scintillation Counting Applied to Chlorine-36

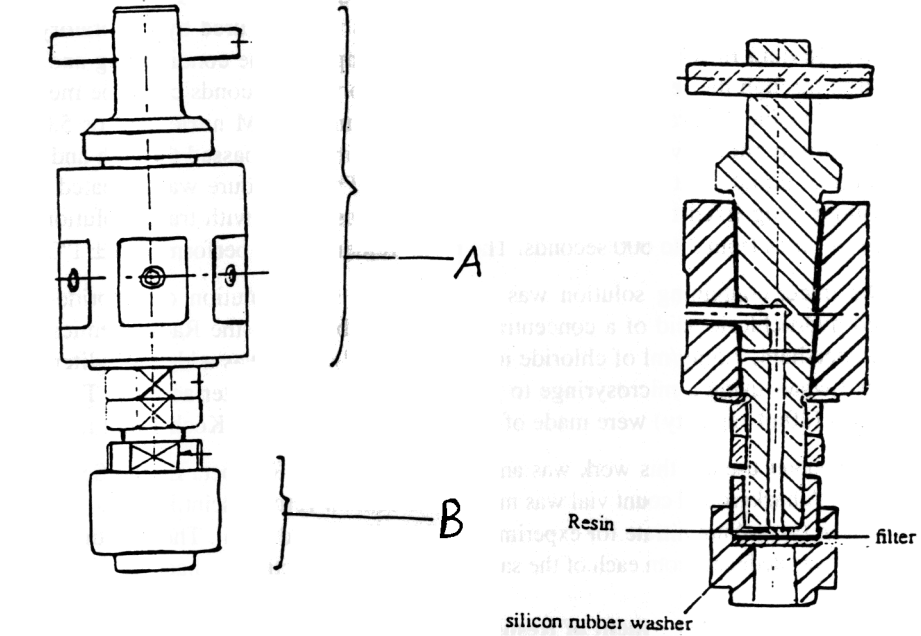
The scintillation counting technique used for radioactivity measurement depends on the interaction of nuclear radiation with matter, producing light in the near UV or visible part of the spectrum. Chlorine-36 which is used in this work, has a half-life of  $3.1 \times 10^5$  y and  $\beta$ -particle end-point energy of 0.71 MeV<sup>[9]</sup>.

The scintillation cocktail used consisted of 2g of 2,5-diphenyloxazole (PPO), 0.1g of 1,4-di-(2-(5-phenyloxazolyl)) benzene (POPOP) and 30g of naphthalene (all Scintillation grade chemicals, Fisons, Loughborough, Leicestershire, England, U.K.) dissolved in 500ml of 1,4 dioxane (Fisons, Scintillation grade). A 50ml portion of methanol (Koch-Light Laboratory, Coinbrook, Slough, Berkshire, England, U.K.) and 10ml of ethyleneglycol (Fisons, A.R) were added to the cocktail. A magnetic stirrer was used for about three hours to effect the solution. Finally, solvent saturated nitrogen gas was bubbled through slowly to remove dissolved oxygen from the cocktail.

### Experimental

The apparatus used is similar to that described by Boyd *et al.*<sup>[3]</sup> and is shown in Fig. 1. The 4-way stop-cock, (A) consisted of a PTFE body with four inlets, having a tapered KEL-F core and had a single inlet, as shown. The cell in which the resin was held (B) screwed onto the stopcock core. It was made of KEL-F, and divided into two parts

which screwed together. A filter was held between the two parts and was sealed by a silicon rubber washer. The filter was a disk of 0.013mm thickness and 13mm in diameter cut from a 3M/8500 non-toxic Particle Mask (Whatman) subjected to 10 tons/in<sup>2</sup> pressure by means of hydraulic press (C-30, Research and Industrial Company, London, England) so that it was slightly larger in diameter than the bore of the cell. A fresh filter was used with each batch of resin.



Conditioning solution reservoir

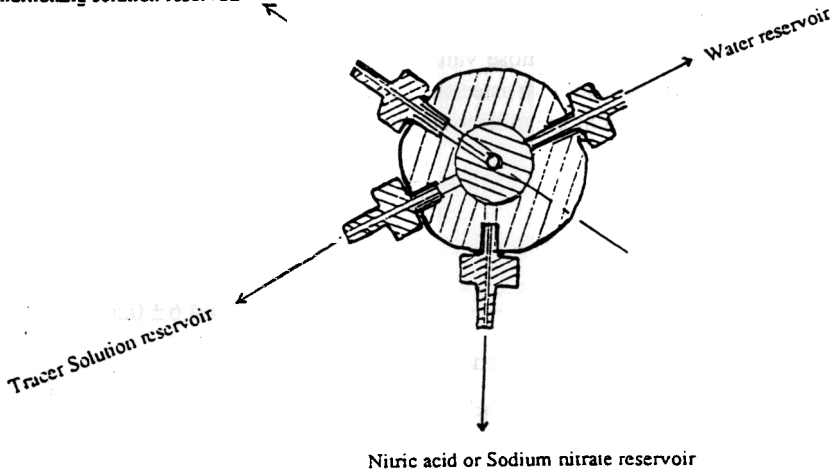


FIG. 1. Apparatus for Shallow Bed Technique.

A weighted sample of resin (10 to 20mg) was placed in the cell and initially flushed with deionized water to wet it and remove air bubbles. It was then eluted with conditioning solution for about ten minutes at a constant flow rate (3.0ml/min) to achieve equilibrium. This solution had the same composition as the solution containing the labelled chloride, but was inactive.

An active solution was then passed through the bed for a specified time at a constant flow rate (3.0ml/min). Two Milton Roy mini-pumps manufactured by Laboratory Data Control Riviera Beach, Fl, U.S.A., were used to pump both the conditioning and tracer solution through the resin bed. Time intervals as short as 3 seconds could be measured with reasonable accuracy. Finally, 5.0ml of approximately 4M nitric acid or 5.0ml of 0.5M sodium nitrate (when using the silica-based resin) were passed through and added to 15ml of liquid scintillant for counting purposes. The procedure was repeated for increasingly long fixed times. Thus, the same resin was eluted with tracer solution for a range of times from 3 to 600 seconds. The measurements were performed at  $\pm 1^\circ\text{C}$ .

The tracer-containing solution was made from a stock solution of chloride-36 labelled hydrochloric acid of a concentration taken to be 0.2M (the Radiochemical Centre, Amersham, 7.5mg/ml of chloride ion,  $103\mu\text{Ci/ml}$ ).  $50\mu\text{l}$  was added to 1 liter of deionized water using a microsyringe to give a solution of  $5\mu\text{Ci/liter}$  activity. The counting vials (20ml capacity) were made of polyethylene supplied by Koch-Light Ltd.

The counter used in this work was an L.K.B.-Wallc 1215 Rackbeta Liquid Scintillation Counter. A background count vial was made up to contain 15ml of scintillant and 5ml (4M) nitric acid (or sodium nitrate for experiments with silica based resin). The counting rate for this vial was deduced from each of the sample vials as a correction for background activity.

### Treatment of Results and Discussion of Errors

For each resin, the counting rate per unit weight (specific counting rate) expressed as counts per minute CPM per mg,  $R$ , is tabulated as a function of time in seconds. From a plot of  $R$  against time,  $t$ , the counting rate per mg beyond which equilibrium exchange has been attained is estimated. Those values for which the specific counting rate is independent of time are marked with asterisk. The average of these  $R$  values is taken to be  $R_\infty$ . The fractional attainment of equilibrium,  $F$ , is then calculated from the relation

$$F = \frac{R_t}{R_\infty}$$

Example, Table for  $t = 10$ ,  $R_t = 1.5$

$$R_\infty = \frac{4.6 + 4.3 + 4.3 + 4.5 + 4.4 + 3.9 + 5.4 + 5.4}{8} = 4.6 \pm 0.5$$

where the error quoted is the standard deviation of the mean

$$F = \frac{1.5}{4.6} = 0.33$$

$\sqrt{t} = \sqrt{10} = 3.2$  and  $-\ln(1-F) = -\ln(1-0.33) = 0.40$  are then readily calculated. The reaction half-time, *i.e.* the time required for  $F$  to attain a value of 0.5 can be read from a

plot of  $F$  against  $t$  (Fig. 2) From data in Table 1 and Fig. 3,  $t_{1/2}$  has a value of 24 second. Each value of  $F$  and  $-\ln(1-F)$  is obtained using  $R_{\infty}$  so that an error in  $R_{\infty}$  would reflect on the shape of the plots of  $F$  against  $\sqrt{t}$  (Fig. 4) and  $-\ln(1-F)$  against  $t$  (Fig. 5).

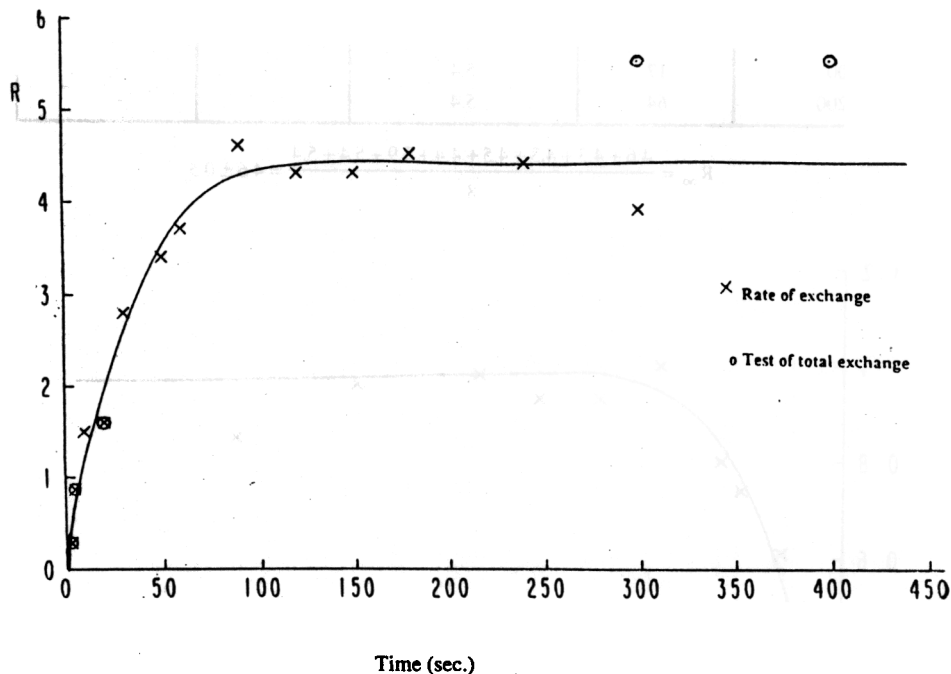


FIG. 2. Counting rate,  $R$ , against time for XAD-2 resin functionalised with CMEE and TMA.

TABLE 1. XAD-2 resin functionalized with chloromethyl ethyl ether (CMEE) and trimethylamine (TMA). Particle size: 30-40 $\mu$ m; exchange capacity 0.014 meq./g.

Time (sec)	$\sqrt{t}$	CPM / mg (R)	F	$-\ln(1-F)$
3.0	1.7	0.29	0.063	0.07
5.0	2.2	0.87	0.19	0.21
10	3.2	1.5	0.33	0.40
20	4.5	1.6	0.35	0.34
30	5.5	2.8	0.61	0.94
50	7.1	3.4	0.74	1.35
60	7.7	3.7	0.80	-
*90	9.5	4.6	1.0	-
*120	11	4.3	0.93	-
*150	12	4.3	0.93	-
*180	13	4.5	0.98	-
*240	15	4.4	0.96	-
*300	17	3.9	0.85	-

Test for total exchange

Time (sec)	$\sqrt{t}$	CPM / mg (R)	F	$-\ln(1-F)$
3.0	1.7	0.31	0.067	0.07
5.0	2.2	0.74	0.16	0.17
20	4.5	1.6	0.35	0.43
*300	17	5.4	-	-
*4200	64	5.4	-	-

$$R_{\infty} = \frac{4.6 + 4.3 + 4.3 + 4.5 + 4.4 + 3.9 + 5.4 + 5.4}{8} = 4.6 \pm 0.5$$

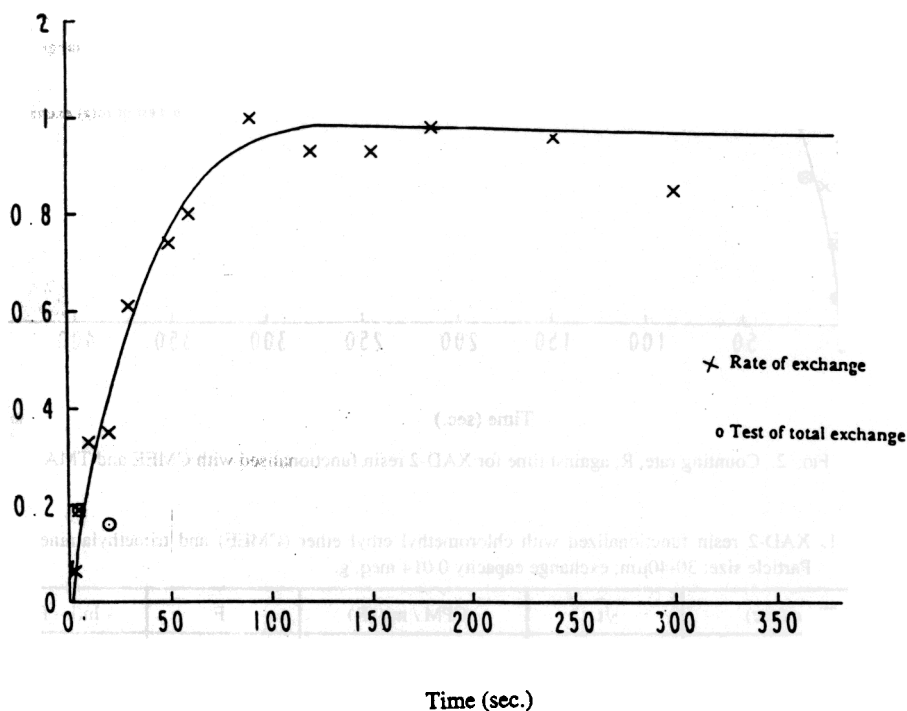


FIG. 3. Fraction, F, against time for XAD-2 resin functionalised with CMEE and TMA.

In the plots for the  $-\ln(1-F)$  function of  $t$ , as  $F \rightarrow 1$  the errors increase rapidly so that the value for  $t > 120$  second are unreliable. The error in  $1-F$  rises steeply. For an uncertainty of 18%, values of  $F$  beyond  $F = 0.66$  in the data set taken here will give unreliable misleading results. Thus, the plot  $-\ln(1-F)$  against  $t$  should not be considered beyond  $t = 120$  seconds. When that is done set data points for the various  $R_{\infty}$  fall on a reasonably smooth-linear curve. Thus, general conclusions regarding the rate controlling process in anion exchange do not appear to depend critically on the  $R_{\infty}$  taken.

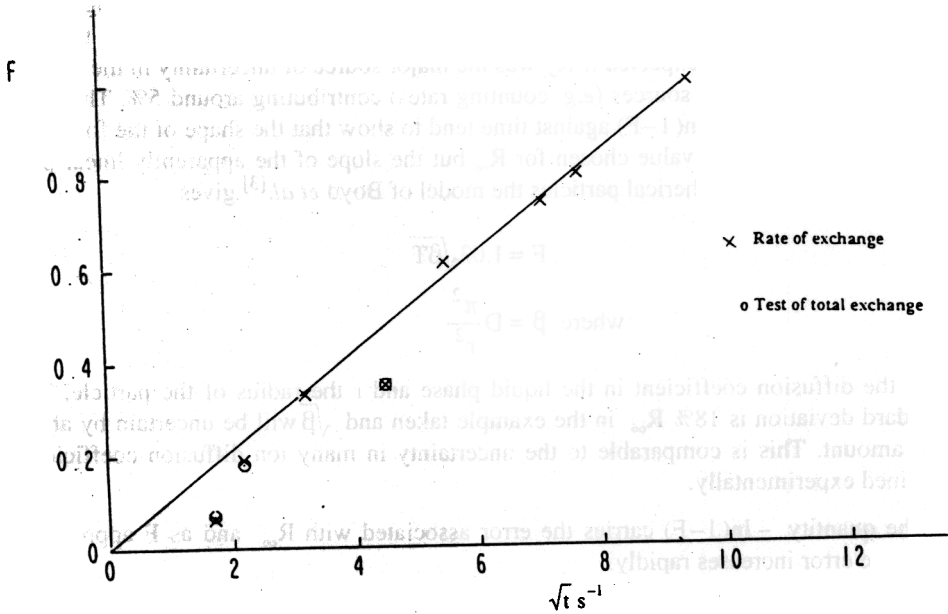


FIG. 4. Fraction, F, against  $\sqrt{t}$  for XAD-2 functionalised with CMEE and TMA.

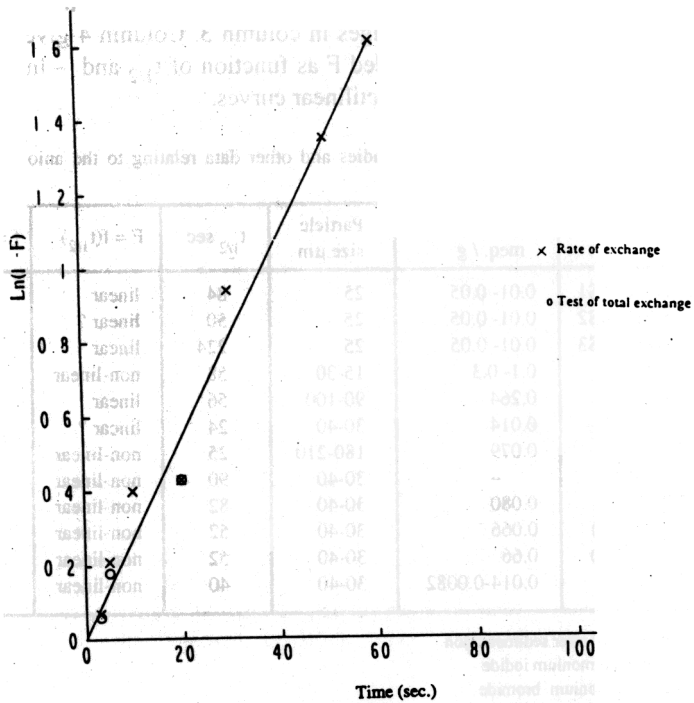


FIG. 5.  $-\ln(1-F)$  against time for XAD-2 resin functionalised with CMEE and TMA.

The times,  $t_{1/2}$  for 50% exchange are read conveniently from a plot of  $F$  against  $t$ . These are 60,84 and 104 second, respectively, *i.e.* around  $\pm 22\%$  different from the median value as would be expected if  $R_{\infty}$  was the major source of uncertainty in the plotted data (Fig. 3) with other sources (*e.g.* counting rates) contributing around 5%. The plots of  $F$  against  $\sqrt{t}$  and  $-\ln(1-F)$  against time tend to show that the shape of the former is quite insensitive to the value chosen for  $R_{\infty}$  but the slope of the apparently linear portion will change. For spherical particles the model of Boyd *et al.*<sup>[3]</sup> gives

$$F = 1.03\sqrt{\beta T}$$

$$\text{where } \beta = D \frac{\pi^2}{r^2}$$

$D$  is the diffusion coefficient in the liquid phase and  $r$  the radius of the particle. The standard deviation is 18%  $R_{\infty}$  in the example taken and  $\sqrt{\beta}$  will be uncertain by about that amount. This is comparable to the uncertainty in many ion diffusion coefficients obtained experimentally.

The quantity  $-\ln(1-F)$  carries the error associated with  $R_{\infty}$  and as  $F$  approaches unity the error increases rapidly.

### Discussion of Results

The data from the rate studies are summarized in Table 2 along with the exchange capacity in column 2 and particle size ranges in column 3. Column 4 gives the exchange half-times while column 5 and 6 recorded  $F$  as function of  $t_{1/2}$  and  $-\ln(1-F)$  as function of  $t$  in terms of rectilinear or non-rectilinear curves.

TABLE 2. Summary of the results of the rate studies and other data relating to the anion exchanging substances.

	Ion exchanger	Capacity meq. / g	Particle size $\mu\text{m}$	$t_{1/2}$ sec	$F = f(t_{1/2})$	$f = (t) = \ln(1-F)$
1	Dionex HPIC-AS1	0.01-0.05	25	84	linear	non-linear
2	Dionex HPIC-AS2	0.01-0.05	25	50	linear ?	linear ?
3	Dionex HPIC-AS3	0.01-0.05	25	224	linear	non-linear
4	Vydac 302	0.1-0.3	15-30	58	non-linear	linear
5	XAD-2 FUNCT.	0.264	90-100	56	linear	non-linear
6	XAD-2 FUNCT.	0.014	30-40	24	linear ?	linear ?
7	XAD-2 TLMAl.	0.079	180-210	25	non-linear	linear
8	XAD-2 TLMAl.	-	30-40	90	non-linear	linear
9	XAD-2 TLMAl.	0.080	30-40	82	non-linear	linear
10	XAD-2 CTAB(a)	0.066	30-40	52	non-linear	linear
11	XAD-2 CTAB(b)	0.66	30-40	52	non-linear	linear
12	XAD-2 CTAB	0.014-0.0082	30-40	40	non-linear	non-linear

(a) Before sedimentation, (b) after sedimentation

TLMAl = tri-laurylmethylammonium iodide

CTAB = cetyltrimethylammonium bromide

The XAD-2 resin products were functionalized as described in ref. [10].



It is convenient to consider the Dionex and Vydac exchangers first because they were studied in the form of spherical particles and therefore may be expected to conform in behaviour more closely to conditions specified in the model used by Boyd *et al.*<sup>[3]</sup> to derive the functions enabling us to distinguish between particle and film diffusion rate controlling mechanisms. However, of these four exchangers, it has been seen from the electron micrographs that the first three really consist of very small (about 0.1  $\mu\text{m}$  diameter) approximately spherical particles agglomerated on the surface of much larger (25 $\mu\text{m}$  diameter) spheres. In the case of AS2 resin, the particles are uniformly 0.1 $\mu\text{m}$  in diameter and its rate does not permit a distinction to be made between the two mechanisms. For AS1 and AS2 particle diffusion control of the rate of exchange is favoured.

The Vydac 302 exchanger consists of hydrocarbon chain chemically bonded to a spherical particle of mean particle diameter 20 $\mu\text{m}$  and pore diameter 330 $\text{\AA}$ . The functional groups are within the large pores of the particles and they are expected to be immersed in the static liquid water medium not much affected by the flow of mobile phase over the particles. For Vydac 302 either film diffusion or the ion exchange process could be the rate controlling. The data for the functionalized XAD-2 resin show that the particle diffusion control or chemical exchange is rate determining for the larger particle/higher capacity sample. It might be expected that particle diffusion control would apply to these large particles and such high capacity materials. Unfortunately, the data for low capacity smaller particles do not give a clear distinction between the possible mechanisms.

Turning to the coated resin (Number 7 to 12) it is seen that the results are inconclusive for 12. The inconclusive result for 12 may be due to a decreasing exchange capacity with time as observed from regeneration steps. For 7, 8, 9, 10 and 11 it is seen that film diffusion or chemical exchange rate control would appear to be consistent with the data.

**Acknowledgement:** The work contained here was performed at The University of Kent, Canterbury, England, and I record my thanks to Prof. S.J. Lyle for supervision and advice during the work and in the preparation of this paper.

#### References

- [1] Small, H., *Ion Chromatography*, Plenum Press, New York (1989).
- [2] Helfferich, F., *Ion Exchange*, McGraw-Hill, New York (1962).
- [3] Boyd, G.E., Adamson, A.W. and Myers, L.S. Jr., *J. Am. Chem. Soc.*, (1947) **69**, 2836.
- [4] Turse, R. and Rieman, W., *J. Phys. Chem.* (1961), **65**, 1821.
- [5] Heitner-Wirguin, C. and Markovits, G.J., *J. Phys. Chem.* (1963), **67**, 2263.
- [6] Schwartz, A., Marinsky, J.A. and Spiegler, K.S., *J. Phys. Chem.* (1964), **68**, 918.
- [7] Varon, A. and Rieman, W., *J. Phys. Chem.* (1964), **68**, 2716.
- [8] Helfferich, F., *Ion Exchange and Solvent Extraction*, vol. 1 Chap. 2, Marinsky, J.A. and Marcus, R. (Ed.), Marcel Dekker, New York (1966).
- [9] Dyer, A., *An Introduction to Liquid Scintillation Counting*, Heyden, London (1974).
- [10] Gerde, D.T. and Fritz, J.S., *J. Chromatog.* (1979), **176**, 199.

## معدل الانتشار التبادلي في المبادلات الأيونية منخفضة السعة التبادلية

صالح بن عمر سعيد باحفي

قسم الكيمياء ، كلية العلوم ، جامعة الملك عبد العزيز

جدة - المملكة العربية السعودية

المستخلص . تهدف الدراسة إلى معرفة نوع الانتشار الأيوني في حبيبات المعادلات الأيونية منخفضة السعة التبادلية .

والانتشار نوعان هما :

١- انتشار داخل الحبيبات .

٢- انتشار داخل الطبقة الرقيقة من السائل التي تحيط بالحبيبات

ولمعرفة نوع الانتشار فقد استخدم جهاز شالو (الشكل ١) حسب الخطوات التالية :

١- تؤخذ ١٠-٢٠ ملليجرام من المبادل الأيوني وتوضع في الوحدة B من الجهاز .

٢- يحول المبادل إلى صيغة الكلوريد وذلك بإمرار حامض الهيدروكلوريك المخفف تركيز  $1 \times 10^{-5}$  مول/ لتر بمعدل ٣ مل/ دقيقة باستخدام مضخة خاصة وفترات زمنية محددة .

٣- يمرر محلول الكلور المشع (كلور ٣٦) تركيز ٥ ميكروكوري بنفس المعدل السابق ونفس الفترات الزمنية المحددة فيحل الكلور المشع محل الكلور غير المشع .

٤- يمرر محلول حامض التتريك أو نترات الصوديوم فيحل أيون التترات محل الكلور المشع الذي يستقبل في زجاجة تحتوي على محلول مومض ثم يقاس الكلور المشع باستخدام جهاز لقياس الإشعاع .

الدراسة تحتوي على نتائج لعدة مبادلات أيونية تتضمن بعض الراتنجات من شركة دايونكس .