The Rate of Swelling of Ion-Exchange Resin Particles in Different Salt Solutions

CARLOS PULIDO*

Institute of Physical Chemistry, University of Uppsala, Sweden

This note has been published mainly to point out the possibilities of the photographic method used and to show the length of time required for volume changes of ion exchange resin particles due to exchange of ions. Figures 5 to 10 are self-explanatory and it is seen that there is a marked difference in behaviour of the resin for different types of ions and valencies. It is also seen that the time required for these volume changes is such that they can be conveniently followed by the method used. As it seems of interest from many points of view to study the kinetic properties of ionic exchange resins in more detail in this way, a systematic investigation has now been undertaken and it has been found that the pretreatment of the resin is of the greatest importance in determining its behaviour.

Several papers have been presented during the last few years on the study of the swelling of ion-exchange resins, as well as on the diffusion of solutions in these resins. These, however, have dealt with columns or beds of resins.

Thus Boyd *et al.*[1] have used the same shallow bed arrangement used by Domaine *et al.*[2] The amount of exchanger they used was 100 mg or 10 mg depending on the concentration of the solutions. When the amount was 10 mg the shallow bed was a cylinder, roughly three particle diameters deep and about twenty particles in diameter. Hale and Reichenberg[3] have used a modification of Boyd's method[1] or, in the case of sulphonated cross-linked polystyrene, another method in which the hydrogen form of the resin was stirred with a solution in the presence of an indicator. Kressman and Kitchener[4] have employed for their experiments the limited bath method with a large number of particles — about 500.

Many other papers have been published on this subject but in all of them the resins were studied in quantities of at least about a hundred particles.

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* Present address: Centros de Estudos da Energia Nuclear, Instituto Superior Técnico, Lisboa, Portugal.

Therefore it should be interesting to study the individual behaviour of the resin particles, and work is being carried on with this aim in view. The purpose of this paper is to present the first results.

RELATION BETWEEN SWELLING AND DIFFUSION

According to Boyd, Adamson and Myers [1], there are three principal stages to be considered in the mechanism of swelling, and each of them may be rate-controlling under appropriate conditions:

I. Diffusion of ions through a thin film of liquid surrounding the particles (or through liquid in macropores inside the particles).

II. Diffusion of ions through the resin material itself.

III. The chemical process of exchange.

However, diffusion in and through the solid material is rate-determining for the more concentrated solutions [1], about 0.1 N.

As the exchange reaction is accompanied by a change of volume, this change should be related to the diffusion inside the particles for concentrations in which this diffusion is rate-controlling. Actually, using 0.5 M solutions, values were found for the swelling of the particles which substantiated this relation.

MATHEMATICAL EQUATIONS

The diffusion of a liquid inside the spherical particles follows the same law as that of the heat transport in spheres [5].

The appropriate equation is

$$\frac{\partial u}{\partial t} = D^i \left(\frac{\partial^2 u}{\partial x^2} \right) \tag{1}$$

where

$u = C^s r$

r = radius of the spherical surface at a concentration C^s in the solid

D^i = internal diffusion coefficient

The solution of this equation was given by Barrer [6] and by Boyd [1]

$$C^s = kC^l + \frac{1}{r} (k \ C^l - C^s{}_0) \frac{2r_0}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi r}{r_0} \cdot e^{-D^i n^2 t / r_0^2} \tag{2}$$

where

k = the distribution coefficient defined by $C^s{}_e = k \ C^l{}_e$

$C^s{}_e$ = the equilibrium concentration in the solid

$C^l{}_e$ = the equilibrium concentration in the liquid

$C^s{}_0$ = the initial concentration of adsorbate in the solid

r = the radius of the spherical adsorbent particle

r_0 = the initial radius of the spherical adsorbent particle.

The rate of permeation, P, i. e. the quantity transferred/unit time/unit area of unit thickness under a standard concentration difference is

$$P = - D^i \left(\frac{C^s}{r} \right)_{r=r_0} \tag{3}$$

and the total quantity of solution which crosses the unity of area in the time t is:

$$q = \int_0^t P \, dt \qquad (4)$$

Supposing the initial concentration in the solid is zero, we obtain, from eqns. (2), (3) and (4)

$$q = \frac{2r_0}{\pi^2} \, k \, C^1 \left[\sum_{n=1}^{\infty} \frac{1}{n^2} \, e^{-D^i n^2 \pi^2 t / r_0^2} - \sum_{n=1}^{\infty} \frac{1}{n^2} \right] \qquad (5)$$

The total quantity adsorbed, will be:

$$Q = 4 \, \pi \, r_0^2 \, q \qquad (6)$$

and Q_∞ being the amount adsorbed at equilibrium $(t = \infty)$, the expression for the fractional attainment of equilibrium, may be written [1]

$$F = \frac{Q}{Q_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \, e^{-D^i \pi^2 n^2 t / r_0^2} \qquad (7)$$

since

$$\sum_{n=1}^{\infty} \frac{1}{n^2} = \frac{\pi^2}{6}$$

Boyd [1] also gives the following solution for cases where the adsorbing particles are not spheres but slabs:

$$F = 1 - \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \, e^{-(2n-1)^2 \frac{\pi^2 D^i t}{4 \, x_0^2}}$$

where x_0 is the half-thickness of the slab. However, the equation for the spheres is more in agreement with experimental data.

Fig. 1 shows the curve corresponding to the equation (7) in which $\frac{D^i}{r_0^2}$ has the value 0.74×10^{-2}.

EXPERIMENTAL

a) *Preparation of materials.* A sulphonated cross-linked polystyrene ion-exchanger was employed. This synthetic resin showed great swelling owing to the low level of cross-linkage. The particles were air dried and granulometrically classified and a few spherical grains with diameters between 0.1 and 0.2 mm were taken from it. The following process was used for the choice of these grains:

A few grains were taken and placed on a slanted plate of glass or polished metal. Tapping gently on the plate, the spherical particles rolled down while the others remained on the plate.
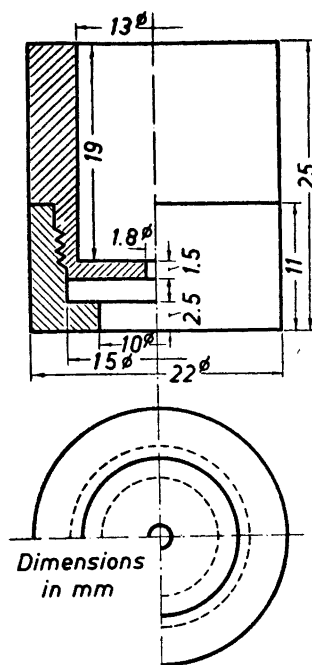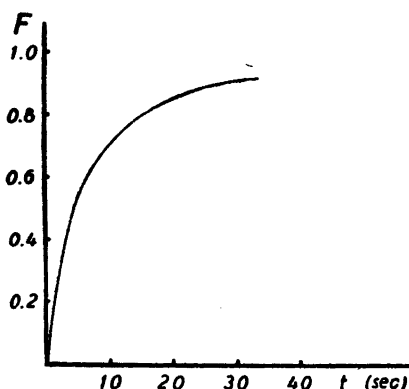
Fig. 1. Curve corresponding to eqn. (7).   *Fig. 2. Cylindrical cell containing the resin.*

The spherical particles were gathered into a small container and were prepared as follows: washed, first with HCl, then with distilled water and finally with NaCl. This process was repeated and the particles were then placed in a small cylindrical cell (Fig. 2).

b) *Experimental procedure.* The rate of swelling was determined simply by photographing the particles at regular time intervals. The instrument employed to obtain the values of swelling is shown in Fig. 3.

A known number of spherical particles of resin was placed in the cell. The excess liquid was taken out by means of a curved pipette leaving only enough to cover the resin particles. By means of another pipette HCl was poured into the cell in such a way as to allow the particles to remain unmoved. They were kept there for 6 to 8 hours and then, using the same process the HCl was taken out and NaCl poured into the cell. After another period of 6 to 8 hours the same technique was repeated for three days running. After this preparation the resin was in good condition for measurements.

The concentration of the solutions was 0.5 M for NaCl, KCl, NH_4Cl, $BaCl_2$ and $LaCl_3$, 0.001 M for $BaCl_2$ and 0.5 M for HCl. The technique used was as follows: A photograph was taken of a known number of resin particles placed in the cell, in a given solution (Fig. 4). Afterwards the upper part of the liquid was taken out leaving only the minimum to keep the particles immersed. The solution containing the cation to exchange was then poured into the cell carefully by means of a curved pipette. The time was counted from the moment this solution came into contact with the resin, and two seconds later the first photograph was taken. More photographs were taken at intervals varying according to the reaction under study.

The system has no shutter as it was handled in a dark room and the exposure time was controlled by the lamp S. The diameters of the particles were thus measured in each
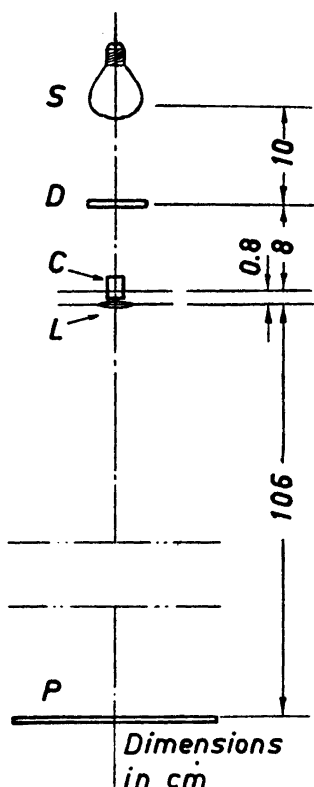
Fig. 3. Arrangement for determination of swelling. S lamp; D diaphragm; C cell containing the resin; L lens; P photographic plate. A 150 w, 220 V normal lamp was used. The lens was a microscope lens which could give a suitable enlargement (about 60 times). The photographic plates used were Gevaert Superchrome 32°. Exposure time about 3/4 sec.
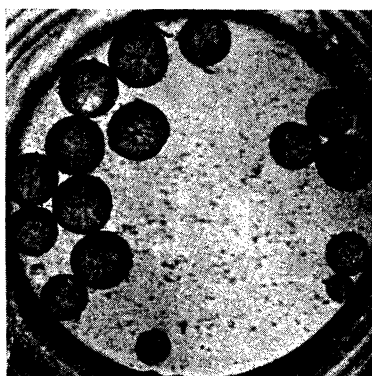
Fig. 4. Resin particles photographed as described in the text.

photograph, provided they had not moved. The average value of the diameters was then computed for each plate. The increasing or decreasing percentage of this average diameter, $\Delta \varnothing$ (%), was then plotted against time.

EXPERIMENTAL CURVES

Figures 5 to 10 show the curves obtained, as explained above, with a synthetic resin of the sulphonated cross-linked polystyrene type and the cations mentioned. In each figure there are two curves, one obtained by measuring the diameters of particles which have first adsorbed hydrogen ions from HCl and then cations to be exchanged from the salt. The other curve was obtained
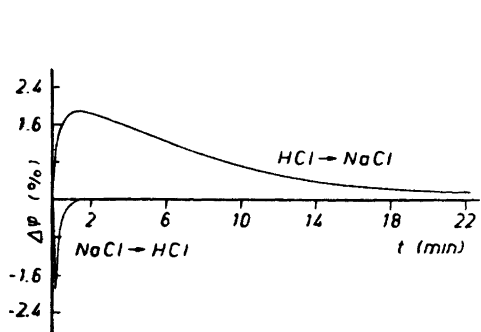
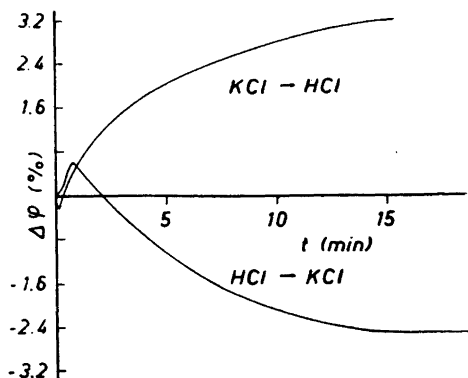**Fig. 5.** *Particles treated with 0.5 M HCl and 0.5 M NaCl.*

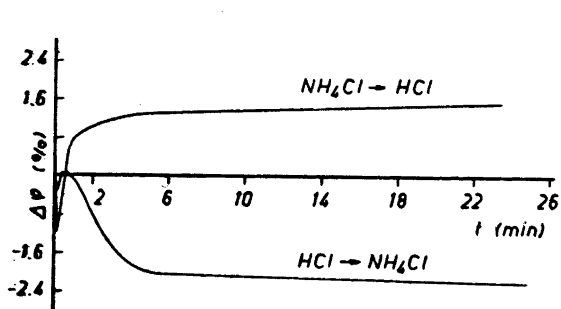**Fig. 6.** *Particles treated with 0.5 M HCl and 0.5 M KCl.*

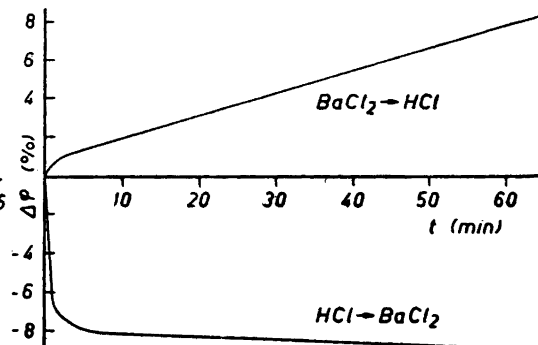**Fig. 7.** *Particles treated with 0.5 M HCl and 0.5 M NH₄Cl.*
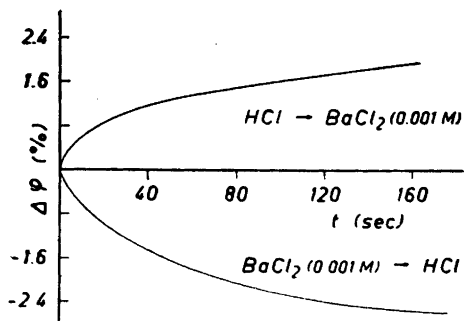
Fig. 8. *Particles treated with 0.5 M HCl and 0.5 M BaCl₂.*

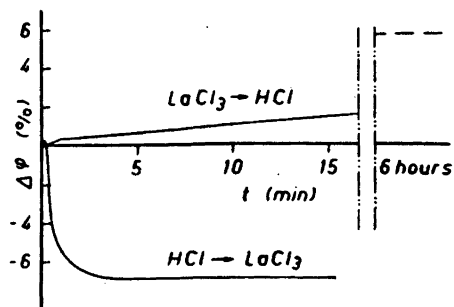**Fig. 9.** *Particles treated with 0.5 M HCl and 0.001 M BaCl₂.*

Fig. 10. *Particles treated with 0.5 M HCl and 0.5 M LaCl₃.*

in the opposite way, *i. e.*, the particles were in a salt solution and a hydrochloric acid solution was added. The statistical deviation range is between 0.08 and 0.1 %.

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