Kinetics of Exchange involving Ion Association on a Weak Acid Resin

By M. B. HANLEY, S. C. CHURMS, and E. C. LEISEGANG

(*Department of Chemistry, University of Cape Town, Cape of Good Hope*)

IN 1963 we obtained kinetic data on the properties of the weak acid resin Amberlite IRC-50 which could not be explained on the basis of the classical theory developed by Boyd *et al.*[1] These workers showed that the kinetics of an ion-exchange process which is particle-diffusion controlled[2] would obey the equation:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2Bt}$$

in which $F = Q_t/Q_\infty$, the fractional attainment of equilibrium of the ingoing (or displacing) ion, where Q_t = number of milliequivalents of the ingoing ion on the resin at time t, and Q_∞ = number of milliequivalents of the ingoing ion on the resin after equilibrium has been reached; $B = \bar{D}\pi^2/r^2$, where $\bar{D}$ = effective diffusion coefficient of the exchanging ions in the resin and r = radius of the resin particle, and t = time.

This equation shows that F is a function of B and t only, that is the rate is proportional to the diffusion coefficient in the resin and inversely proportional to the square of the particle radius. It is independent of the concentration of the ingoing ion, since this term does not appear in the expression and in fact Reichenberg[3] has found this to be the best criterion for characterising particle-diffusion control. It is seen from the equation that for every value of F a value of Bt may be calculated, and *vice versa.* Values of Bt corresponding to various values of F have been tabulated.[3] Thus a convenient method exists for testing whether a process is particle-diffusion controlled. From the Bt against F tables, values of Ct corresponding to the experimental values of F are found. The plots of Bt against t should be linear and pass through the origin if particle diffusion is rate-controlling.

The above test was used by Conway *et al.*[4] for the exchange of sodium for hydrogen on Amberlite IRC-50. These workers demonstrated particle-diffusion control and that the rate of exchange was independent of the ingoing sodium-ion concentration in the range 0·01 to 1·0N.

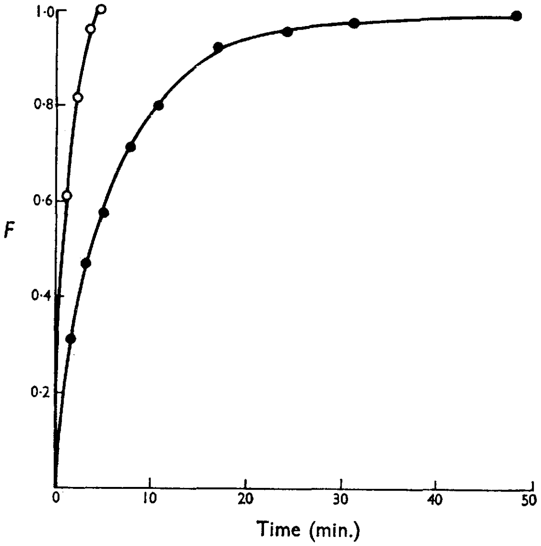

FIGURE 1. *Rate of uptake of hydrogen ions by Amberlite IRC-50 in the sodium form for two hydrogen-ion concentrations,* c, *at* 23°; ● *at* 0·11N, ○ *at* 0·50N.

The reverse reaction, namely the exchange of sodium ions on the same resin for hydrogen from solution has been studied in this laboratory (see Figure 1). Resin of particle size 0·052 to 0·066 cm. diameter, sieved in the air-dry hydrogen form and of moisture content 11% was used. The experimental results were found to conform to the Boyd equation (Figure 2), thus indicating particle-diffusion control. However the rate of uptake of hydrogen ion is clearly dependent upon its concentration in the solution (Figure 1). It is well known[5] that the rate of uptake of co-ions increases with concentration but this was not thought to be the case for counter-ions in reactions which were particle-diffusion controlled. We were therefore at a loss to explain our results.

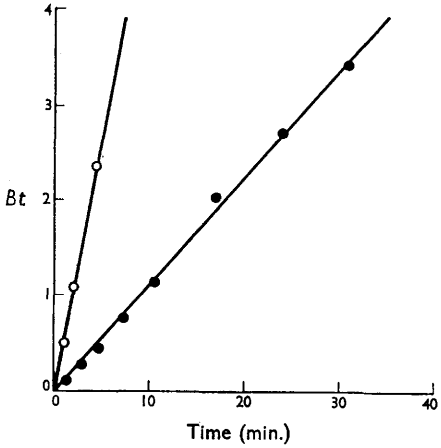

FIGURE 2. *Application of the Boyd equation to the data of Figure* 1.

In 1965 Helfferich[6] predicted theoretically that the rates of ion-exchange processes involving reaction such as association of the ingoing ion with the ionogenic groups of the resin would be found to be concentration-dependent, even where particle diffusion was rate-controlling. This is in contradiction to the conclusion (F independent of concentration of ingoing ion) drawn from the absence of concentration terms in the Boyd equation (in which the effect of association is neglected). Helfferich's Paper gave reasons showing that quantitative rate laws, in the form of explicit equations for ion-exchange processes of this type, were not derivable. It was also stated that Helfferich's predictions were in need of experimental verification.

The present preliminary results clearly show the rate of exchange to be particle-diffusion controlled and yet dependent on the concentration of the ingoing hydrogen ion. These results are believed to provide the only experimental verification hitherto published for these recent theoretical predictions of Helfferich.

(*Received, July* 6*th,* 1966; *Com.* 468.)

---

[1] G. E. Boyd, A. W. Adamson, and L. S. Myers, *J. Amer. Chem. Soc.*, 1947, **69**, 2836.
[2] F. Helfferich, "Ion Exchange", 1st edn., McGraw-Hill Book Co., New York, 1962, ch. 6.
[3] D. Reichenberg, *J. Amer. Chem. Soc.*, 1953, **75**, 589.
[4] D. E. Conway, J. H. S. Green, and D. Reichenberg, *Trans. Faraday Soc.*, 1954, **50**, 511.
[5] E. Glueckauf and R. E. Watts, *Proc. Roy. Soc.*, 1962, *A*,**268**, 339.
[6] F. Helfferich, *J. Phys. Chem.*, 1965, **69**, 1178.