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### The Rate Problem of a Thermally Regenerable Ion-Exchange System

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## The Rate Problem of a Thermally Regenerable Ion-Exchange System

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### SUMMARY

Earlier equilibrium studies have established the thermal dependence of the equilibrium between salt solution and a mixed bed of weakly basic and weakly acidic ion-exchange resins. High resin utilization can be achieved if the resin properties and equilibrium conditions are optimized; the equilibrium characteristics of polyacrylic acid and polyvinylbenzyl-diethylamine resins are quite suited for the practical desalination of brackish waters.

However, the adsorption rates exhibited by normal-sized resin beads of this type are much too slow for satisfactory operation of the process because of the low concentration of protons available for transfer between the resins. It is shown that increasing the porosity of the resins improves amine resin kinetics 10-fold and carboxylic acid resin kinetics 6-fold. Nevertheless such improvements are still inadequate for practical purposes, and it is concluded that for satisfactory rates to be achieved systems having much shorter diffusion paths are necessary.

Two further approaches to the rate problem are discussed, both involving the synthesis of novel resin systems. A mixed bed of microbeads (10-20  $\mu$ ) reacts at acceptable rates but presents mechanical problems; the magnetic

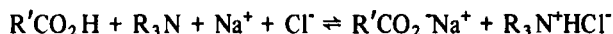
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flocculation of finely divided magnetic resins is reported as one possible solution to this problem. Another avenue is the synthesis of normal-sized beads of the amphoteric and snake-cage variety. Resins of this type that exchange at suitable rates are described.

## INTRODUCTION

This paper describes recent studies in the Sirotherm desalination project, where some unusual properties of polymeric systems are being exploited to achieve thermal regeneration of ion-exchange resins. The ion-exchange reactions which occur are shown in the equilibrium



The available exchange sites are formed by the transfer of protons from the carboxylic acid resin to the tertiary amine resin. Both resins become weaker electrolytes on heating, so that there is a reduction in the number of charged sites and salt is released to the solution.

The equilibrium characteristics of systems containing cross-linked polyacrylic acid and amine resins based on cross-linked polystyrene have been worked out in some detail, and have been shown to be highly dependent on the shapes of the titration curves of the resins [1-3], with better equilibrium properties being obtained when the conditions within the resin favor ion pairing [10]. The degree of ion pairing is governed by the polarity of the resin as a whole; in resins of low polarity the pH buffering ability is increased to a remarkable extent, which results in a high utilization of the resin capacity [3]. The likely biological implications of this finding are discussed elsewhere at this Conference [12]. The equilibrium data obtained have been used to compute the performance of a continuous countercurrent process removing 500 ppm of salt from a feed water containing 1000 ppm of salt, and have been found to be quite favorable. The calculations also show that, under these conditions, there is no advantage to be gained by using product water instead of feed water as the regenerant.

The process can be demonstrated by column operation using a fixed bed of the mixed resin [5]. The original resins studied, while having very good equilibrium properties, proved to exchange much too slowly [6]. To put the process in the practical range, an improvement in rates of at least two orders of magnitude was necessary.

The rate of ion exchange in these systems is directly dependent on the proton and hydroxyl ion concentrations [7]. Since in neutral salt solutions these will both be about  $10^{-7}$  M, slow rates of exchange are not surprising; i.e., there is a low driving force. In all desalination processes a compromise is required between the driving force, which reflects the energy cost, and the magnitude of the interface over which salt or energy traverses, which is related to the capital cost. Since the present process avoids a phase change, it gives promise of low energy costs because of its inherently low driving force, but this must be combined with a means of achieving large interfacial areas if a practical process is to emerge.

Three methods have been employed to achieve this. One is to utilize resins which, like activated carbons, have large internal surface areas. The second method utilizes magnetized resins so that finer particles can be manipulated more readily. The third method uses systems which minimize the diffusion path for protons.

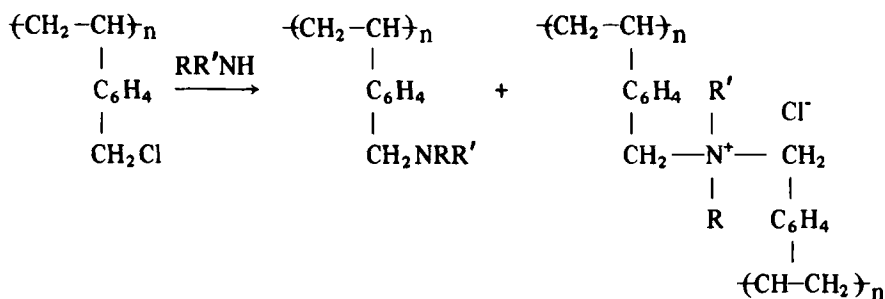
## RESULTS AND DISCUSSION

### I. Normal-Sized Resin Beads (300-1200 $\mu$ diam)

In the first approach a study of the influence of resin structure on adsorption rates was made to determine the factors most likely to accelerate adsorption. A variety of ion exchangers was investigated, as individual resins rather than mixed bed systems, because of the numbers involved.

Measurements were made of the rates of hydrochloric acid uptake by amine resins and of alkali uptake by carboxylic acid resins, using narrow sieved fractions of the beads. The diffusivities were calculated by the method described by Bolto, Kennedy, and Warner [7]. Some of the results obtained are summarized in Tables 1 and 2.

The amine resins shown are all polystyrene-based resins, made by the amination of cross-linked polymer containing chloromethyl groups. Additional cross-links are introduced by a secondary reaction which normally results in about 10% of the total nitrogens being present as quaternary ammonium groups:



The data in Table 1 are for resins having various alkyl groups on the nitrogen. It can be seen that the most pronounced effect is obtained when the gel-type resin initially used (De-Acidite G for which  $D_H$  is  $6.1 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$ ) is replaced by a macroporous resin such as Amberlite IRA-93 or Permutit DEAW-1. The introduction of hydrophilic groups in the remaining gel-type resins is of no great advantage. In the case of hydroxethyl groups (as in Permutit S-1035), there is a slight fall off in rates, and when quaternary ammonium groups are present (as in the De-Acidite H resins) the picture is

**Table 1. Relative Rates of Acid Uptake by Weakly Basic Resins**  
(Particle size: 35-42 Tyler mesh; 1 meq of resin  
in 40 ml of 0.025 N HCl, 0.019 N in NaCl)

Resin	Relative diffusion coefficients	Weak base capacity (meq/g)	Alkyl groups R, R'
De-Acidite G (IP)	1.0	3.9	Both $-\text{C}_2\text{H}_5$
Amberlite IRA-93	10	4.7	Both $-\text{CH}_3$
Permutit DEAW-1	10	2.9	Both $-\text{C}_2\text{H}_5$
Permutit S-1035	0.84	3.8	Both $-\text{C}_2\text{H}_4\text{OH}$
De-Acidite H (IP)			
11% quaternary N	0.85	4.5	Both $-\text{CH}_3$
35% quaternary N	0.26	2.6	Both $-\text{CH}_3$
46% quaternary N	1.1	2.5	Both $-\text{CH}_3$
Permutit MAW-1	0.21	3.4	$-\text{H}$ , $-\text{CH}_3$

**Table 2.** Relative Rates of Alkali Uptake by Weakly Acidic Resins  
(Particle size: 32-35 Tyler mesh;  
2 meq of resin in 40 ml of 0.050 N NaOH,  
0.019 N in NaCl)

Resin	Relative diffusion coefficients	Weak acid capacity (meq/g)
Zeo-Karb 226	1.0	10.4
Amberlite IRC-84	1.0	9.5
Duolite ES-80	2.7	10.6
Lewatit CNP	3.2	10.6
Imac Z-5	3.6	7.3
Permutit 10 HP	3.5	9.5
CSIRO EA-13	5.6	9.5
Permutit SC-1 (8% RSO <sub>3</sub> Na)	1.7	6.1
Permutit SC-4 (36% RSO <sub>3</sub> Na)	0.6	3.5

complicated by the additional cross-linking formed with each ammonium group. The benefit of the extra swelling is only observed in the last member of the series because of the opposing effect of the additional cross-linking. The secondary amine resin Permutit MAW-1 is quite slow because about 30% of the nitrogens have been involved in the cross-linking reaction at the amination stage. Macroporosity is obviously the most important factor studied here, but the diffusivities obtained are still an order of magnitude too low.

Table 2 gives data on polyacrylic acid resins. The variations in diffusivities among the commercial resins can be ascribed to variations in cross-linking and porosity. For Zeo-Karb 226,  $D_{OH}$  is  $1.1 \times 10^{-6}$  cm<sup>2</sup> sec<sup>-1</sup>. Also shown are two specially synthesized porous resins CSIRO EA-13 [8] and Permutit 10 HP. The range of diffusivities is not as large as in the amine resin series, probably because a truly macroporous carboxylic bead has not yet been produced. Building in hydrophilic groups as in the Permutit SC resins, which contain sodium sulfonate sites formed by

sulfonation of the divinylbenzene cross-linking units, is again of little use. In the highly substituted resin, extra bridges in the form of sulfone groups appear to be responsible for the slackening off in rates.

While steps could be taken to improve the porosities of carboxylic acid resins even further, it is very unlikely that such a move would bring about the desired total increase in rates of two orders of magnitude.

## II. Micro Beads ( $<50\mu$ diam)

One sure method of increasing adsorption rates is to decrease the particle size; for diffusion into a sphere, the rate is inversely proportional to  $r^2$ , where  $r$  is the radius of the sphere. Hence if the bead size is reduced from 500 to 50  $\mu$ , a 100-fold improvement in rates will result. The mathematical basis for this has already been outlined, along with the experimental confirmation for the weakly basic resin Amberlite IRA-93 [7].

If the particle size is reduced, however, novel engineering techniques are required to operate the process, since the pressure drop over beds of conventional depth would be prohibitively high, so that very shallow beds would have to be used. In addition, accumulated colloids arising from the feed water would have to be removed periodically by a method other than the conventional backwashing procedure in which the microbeads would merely be washed out with the colloids.

A "mixer-settler" type of contacting equipment is a possible solution, but the slow settling rate of even normal-sized beads is the limiting factor. If the density of the resin is raised by incorporating heavier mineral particles within the beads, settling will be faster, but the volumetric capacity and mechanical strength of the beads decrease when there is a high mineral content. If the inner particles are also ferromagnetic, very much faster settling rates can be achieved by magnetizing the particles since the composite resin beads then flocculate strongly. Acceptable settling rates can be obtained with the incorporation of smaller amounts of the particles if they are magnetic, which results in a negligible change in the volume capacity and mechanical strength of the beads. By agitating the suspension the flocs can be redispersed, so that suitably rapid ion-exchange rates are possible. Magnetic resins therefore combine the rate advantage of fine resins with the rapid settling properties of much coarser particles.

Amine resin beads were made by cross-linking aqueous polyethylenimine with epichlorhydrin using water-in-oil type dispersions. With appropriate oil-soluble surfactants, perfect beads of 5-50  $\mu$  diameter can be made. If very finely divided magnetic particles such as  $\gamma$ -iron oxide are incorporated in the aqueous phase, then provided the particles are pretreated with an

epoxy-substituted silane, beads can be produced in which the magnetic material is completely encapsulated by the resin. It has been shown that the settling rates of such resins are indeed suitably fast when the resin is in the magnetized form, as chain structures develop because of the attraction between the composite beads, which consequently flocculate [9]. The unmagnetized resin does not form flocs. It has also been shown that the adsorption rates for agitated suspensions of resins in the magnetized and unmagnetized forms are the same.

Unfortunately, the amine resin described here does not have the best equilibrium properties for thermal regeneration. This is because it contains hydroxy groups and a mixture of primary, secondary, and tertiary amino groups, having different levels of basicity [10, 3]. The preparation of a homofunctional magnetic resin having a nonpolar network is a more difficult synthetic problem. However, the magnetic resin technique should prove extremely useful in chemically regenerated systems as well since faster adsorption rates will mean the use of less resin. It may be necessary to protect the magnetic particles by treatment with suitably substituted silanes to make them resistant to attack by strongly acidic solutions. Magnetic resins also open up many possibilities for continuous countercurrent operation.

### III. Normal-Sized Beads Incorporating Short Diffusion Paths

Beads of normal size, but constructed such that the diffusion paths for proton transfer are much shorter, can be made by including both the required types of groups within the one particle. For example, an amphoteric resin can be made by reacting chloromethylated polystyrene beads with piperidine-4-carboxylic acid (isonipecotic acid). Snake-cage resins are another suitable type. These are made by polymerizing acrylic acid within cross-linked amine resin beads to produce linear polyacrylic acid "snakes" intertwined and entrapped with an amine resin "cage" [11]. The properties of these two types of resin are compared with those of mixed bed systems in Table 3. The effective capacities are measurements of the capacity which can be utilized between 20 and 80°C; they are highest for the mixed beds. The other resins all have a much lower performance, suggesting strong interaction between carboxyl and amino groups, now in very close proximity to one another. The best result is for a snake-cage resin based on the macroporous amine resin Amberlite IRA-93, in which the linear acid snakes may have accumulated within the pores.



**Table 3. Properties of Thermally Regenerable Systems**

Resin system	Effective capacity (meq/g)	Resin ratio, $\frac{\text{available CO}_2 \text{ H}}{\text{available N}}$
<b>Mixed bed</b>		
De-Acidite G/Zeo-Karb 226	1.1	2.5
Amberlite IRA-93/Zeo-Karb 226	1.0	2.5
<b>Amphoteric</b>		
Isonipecotic acid resin based on Permutit chloromethylated beads	0.02	1.0
<b>Snake-cage</b>		
"Cage" incorporating linear polyacrylic acid "snake":		
De-Acidite G	0.04	2.3
De-Acidite G	0.02	1.1
Amberlite IRA-93	0.2	1.1

### COMPARISON OF THE THREE APPROACHES

The rates of salt uptake by some of these systems, as measured in a stirred reactor, are shown in Fig. 1. The results conveniently summarize the outcome of the three approaches. The rate for the original mixed bed of normal-sized resins is given by the slowest curve. If a macroporous amine resin is used instead of the gel type, a slight but inadequate improvement occurs. The two systems for which suitably rapid rates have been successfully achieved are the mixed bed of micro resins (10-20  $\mu$  in size), and the snake-cage resin of normal bead size, comprising linear polyacrylic acid within a macroporous amine resin.

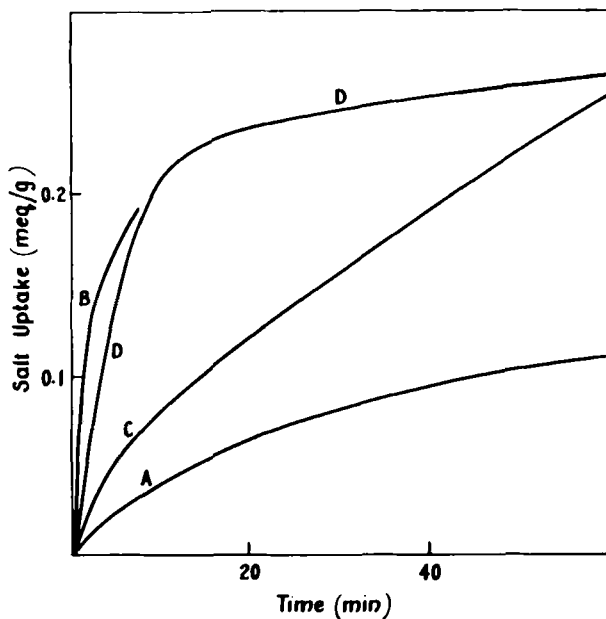


Fig. 1. Rates of salt uptake by some weak-electrolyte resin systems. A, mixed bed of De-Acidite G and Zeo-Karb 226 (300-1200  $\mu$ ). B, mixed bed of De-Acidite G and Zeo-Karb 226 (10-20  $\mu$ ). C, mixed bed of Amberlite IRA-93 and Zeo-Karb 226 (300-1200  $\mu$ ). D, snake-cage resin from Amberlite IRA-93 and polyacrylic acid (300-1200  $\mu$ ).

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