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# ESTIMATION OF ION-EXCHANGE PROCESS LIMITS BY SELECTIVITY CALCULATIONS

## II. REGENERATION CURVES

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SUMMARY

Whether the equilibrium front for an ion-exchange separation will be self-sharpening or non-sharpening can be predicted from resin and solution properties. For self-sharpening fronts, breakthrough inflection, final resin composition and initial leakage can be estimated. For non-sharpening fronts, the Walter equation allows the estimation of initial breakthrough and volume to column saturation. The Walter equation can also be used to construct a curve of degree of regeneration *versus* amount of regenerant used when a selectivity coefficient is available for the system.

Application of these concepts to chemical processing is illustrated by the construction of a regeneration curve from equilibrium data, and estimation of relative performance of two strong-base resins.

INTRODUCTION

Breakthrough curves can be visualized as having two components. The equilibrium component determines the maximum sharpness of breakthrough. The kinetic component only tends to distort the curve from this maximum sharpness. The shape of the equilibrium breakthrough curve is determined by the separation factor between the incoming ion and the ion on the resin. In exchanges between monovalent ions, the separation factor, $\alpha_{AB}$, is identical to the selectivity coefficient, $K_{AB}$.

When the separation factor for incoming ion over the ion being displaced is greater than unity, the equilibrium breakthrough curve is self-sharpening. For self-sharpening curves, breakthrough inflection, final resin composition, and initial leakage can be estimated from resin properties and influent composition using mass–action relationships[1].

In most commercial processes with fully ionized resins, exhaustion occurs with a self-sharpening front and a high percentage of the regenerated capacity is realized before breakthrough of incoming ion. However, regeneration usually involves a non-sharpening front, and full regeneration is achieved only at the cost of excess regenerant. A plot of operating capacity *versus* regenerant dosage is pivotal in presentation of performance data on strong-acid or strong-base resins. In essence,

such a plot shows the degree of regeneration as a function of the amount of regenerant applied per volume of resin. Regeneration curves can be constructed from the separation factor in the exchange by use of an integrated form of the Walter equation[2].

THEORY

In column exchange in which the separation factor is less than unity, the column front is non-sharpening. The equilibrium breakthrough curve is dependent on the exchange capacity of the column and the separation factor in the exchange. This relationship is described by the Walter equation[2]:

$$x_i = \frac{1/a - \sqrt{1/a\tau}}{1/a - 1} \tag{1}$$

where: $x_i$ = equivalent fraction of incoming ion in effluent;
$\quad\quad a$ = separation factor;
$\quad\quad \tau$ = equivalents of incoming ion passed through column divided by capacity of column.

When concerned with regeneration of resin, the effluent history of the ion being displaced is of more interest than that of the influent ion. At any point during the elution the regenerated capacity of the resin is equal to the total equivalents of displaced ion that have left the column. The equivalent fraction of displaced ion in the effluent, $x_d$, at any point is equal to $1 - x_i$. Thus:

$$x_d = \frac{\sqrt{1/a\tau} - 1}{1/a - 1} \tag{2}$$

Fig. 1 shows a calculated equilibrium elution for an exchange with a separation factor of 0.5. Notice that the only ion in the effluent up to $\tau = a$ is the ion originally on the resin, and that the original ion is completely eluted at $\tau = 1/a$.
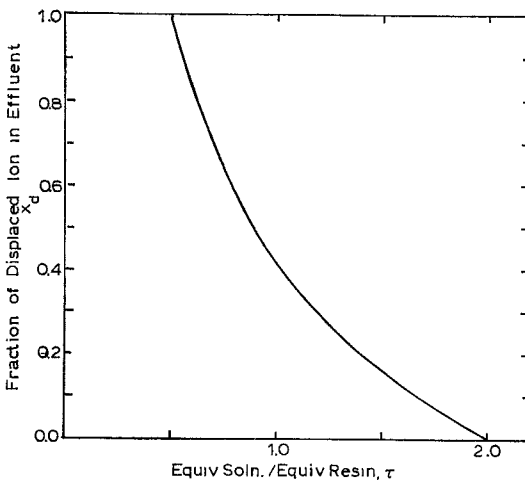


Fig. 1. Elution curve calculated for separation factor of 0.5.

    In establishing practical regeneration conditions the major question is how well the resin is regenerated after the passage of a given amount of regenerant. Or more specifically, what fraction, $\bar{x}_r$, of the resin capacity is regenerated at a given regenerant dosage. This relationship can be obtained from Fig. 1.

    The fraction of the resin regenerated, $\bar{x}_r$, is equal to the sum of the displaced ion equivalents at point $\tau$ divided by the total capacity of the resin. However, since $\tau$ is normalized as equivalents of regenerant ion passed per equivalent of resin, $\bar{x}_r$ is equal to the area under the curve. Thus $\bar{x}_r$ is found by integrating eqn. 2 and solving the definite integral over the limits of 0 to $\tau$. Because the value of the right member of eqn. 2 is not less than unity up to $\tau = \alpha$, the formula for $\bar{x}_r$ in terms of $\alpha$ and $\tau$ becomes:

$$x_r = \alpha + \int_\alpha^\tau \frac{\sqrt{1/\alpha\tau} - 1}{1/\alpha - 1} \, d\tau$$

$$= \frac{2\sqrt{\alpha\tau} - \alpha(\tau + 1)}{1 - \alpha} \tag{3}$$

    Calculation of regenerant dosage must take into account the total capacity of the resin, $\bar{C}$, and the equivalent weight, EW, of the regenerant used.

    regenerant dosage $= (\tau)\,(\bar{C})\,(EW)$ \hfill (4)

    Fig. 2 shows $\bar{x}_r$ *versus* $\tau$ curves for several values of $\alpha$. The displacement of $Na^+$ with $H^+$ from a sulfonated styrene–8% divinylbenzene (DVB) polymer, and the displacement of $Cl^-$ with $OH^-$ from a standard Type II resin both have separation factors of *ca.* 0.65. The displacement of $Cl^-$ with $OH^-$ from a Type I resin (specific water regain $= 0.26$ g/equiv. has an $\alpha$ of only *ca.* 0.06.
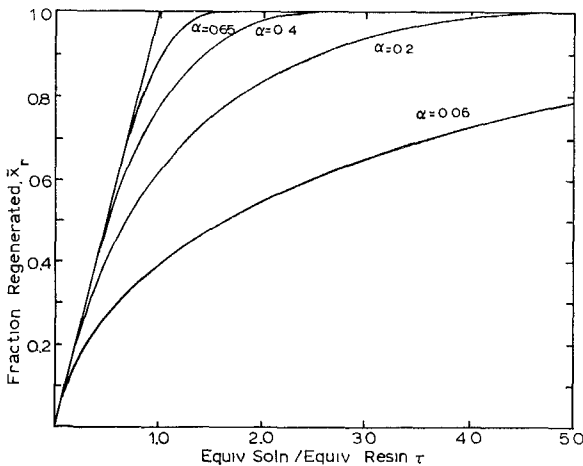


Fig. 2. Degree of regeneration *vs.* dosage.

In Fig. 2 the straight line at slope 1.0 indicates 100% utilization of regenerants. That is, as long as the curve is on this line, every ion of regenerant that enters the column displaces an ion originally on the resin. The $\bar{x}_r$ *versus* $\tau$ curve deviates from the 100% efficiency line at $\tau = \alpha$.

The Walter equation gives effluent composition for a column running under equilibrium conditions. That is, the flow-rate, temperature, bead size, etc., are such that solution and resin phases are at equilibrium at each point in the column. Experimentation has shown that columns with non-sharpening fronts ($\alpha < 1$) approximate equilibrium under reasonable flow conditions[3].

EXPERIMENTAL

A regeneration curve can be obtained in a relatively simple experiment. Assume a resin in B-ion form is to be regenerated to A-ion form with a solution of AY, where Y is the co-ion of the regenerant. A known volume of resin ($\bar{V}$) of known total capacity ($\bar{C}$) is placed in a column. The resin is converted completely into B-ion form and rinsed. The resin is then eluted with a solution of AY and the total effluent collected in cuts of known volume ($v_n$). The concentrations of Y and B are determined in each cut. At each point of the regeneration curve:

$$x_r = \frac{\Sigma\,([B]_n\,v_n)}{CV}$$

$$\tau = \frac{\Sigma\,([Y]_n\,v_n)}{CV}$$

A resin volume of *ca.* 50 ml in a 2 cm I.D. column is satisfactory. An excess of regenerant solution is passed through the column at a flow-rate of *ca.* 5 bed volumes per hour. Cuts are sized to give 5–15 fractions across the exchange. The most convenient analytical technique available is used to determine the concentration of A and Y, B and Y, or A and B in each cut. It is important that the total exchange capacity in the column ($\bar{C}\,\bar{V}$) be known accurately. If the exchange is stoichiometric, at complete elution $\Sigma([B]_n\,v_n) = \bar{C}\,\bar{V}$.

Fig. 3 shows the displacement of sodium ion with hydrogen ion (1.0 $N$ HCl) on two sulfonated styrene–DVB resins. The curves are calculated from eqn. 3. An $\alpha_{H,Na}$ value of 0.65 gives an excellent fit for the data obtained with a standard 8% DVB gel resin, Duolite C-20®. This is in agreement with the value of 1.5 quoted for the selectivity coefficient of Na$^+$ over H$^+$ on such a resin. An $\alpha_{H,Na}$ value of 0.4 is necessary to fit the data for the macroporous resin, Duolite C-26®. This reflects the increased selectivity for sodium ion resulting from higher crosslinking.

Fig. 4 shows the displacement of Cl$^-$ by OH$^-$ (1.0 $N$ NaOH) on a Type I strong-base resin, Duolite A-101D®. An $\alpha$ value of 0.06 gives a curve which fits the data reasonably well.

ESTIMATION OF RESIN PERFORMANCE

When making preliminary estimates on the feasibility of ion exchange for a new process, often it is not practical to run laboratory data. The construction of an
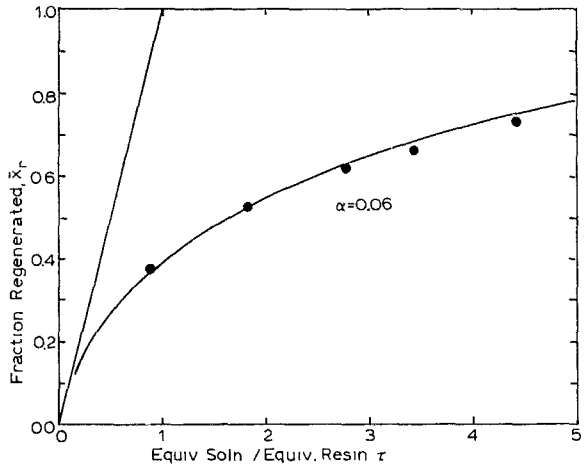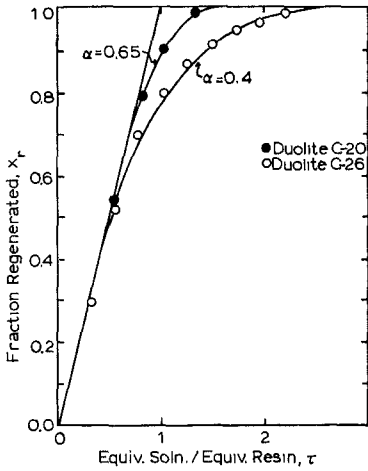
Fig. 3. Elution of $Na^+$ with $H^+$ from sulfonic acid resins.

Fig. 4. Elution of $Cl^-$ with $OH^-$ from type I resin.

approximate regeneration curve may be critical in determining if the process should be considered further. An example is nitrate removal.

Nitrate ion can be removed from potable water by chloride exchange on a strong-base resin. The maximum loading of nitrate can be estimated from the water composition[1,4]. However, the practicality of the process largely depends on finding a practical regeneration level. The selectivity coefficient for nitrate over chloride was originally reported[5] to be *ca.* 4, and this has been substantiated in subsequent work. A separation factor, $\alpha_{Cl,NO_3}$, of 0.25 can be used to construct a regeneration curve using eqn. 3, as shown in Fig. 5. This curve is adequate for setting regeneration levels in determining technical and economic practicability for the process.
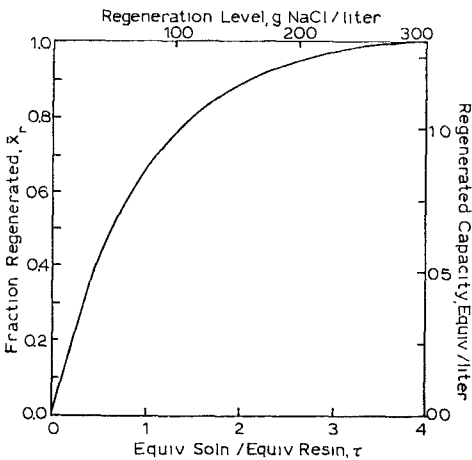


Fig. 5. Estimated regeneration curve for displacement of $NO_3^-$ with $Cl^-$. $\bar{C} = 1.3$ equiv./l; $\alpha = 0.25$.

Eqn. 3 can also be used to determine the relative performance of two resins at a given regeneration level. The operating capacity of a Type I resin in a hydroxide cycle is primarily dependent on how well it is regenerated. The separation factor for $OH^-$ over $Cl^-$ in Type I resins is very dependent on the water balance in the resin, and can be estimated from the resin's specific water regain[6].

Consider two Type I resins with the following properties:

| Resin | H | L |
|---|---|---|
| Wet volume capacity (equiv./l) | 1.2 | 1.5 |
| Dry weight capacity (mequiv./g) | 4.04 | 3.96 |
| Moisture content (%) | 55 | 45 |
| Specific water regain | 0.30 | 0.21 |
| Estimated $\alpha_{OH,C.}$ | 0.08 | 0.04 |

These properties are typical of high and low moisture content grades of Type I resin currently marketed by several manufacturers. In fact, resin H would be considered marginally low in wet volume capacity.

Estimated regeneration curves are shown for those two resins in Fig. 6. Note that for regeneration dosages up to 400 g NaOH/l, resin H shows a higher regenerated capacity and will give a higher operating capacity than resin L even though it has a lower total capacity. Since regeneration dosages seldom exceed 160 g/l, the use of high-capacity, low-moisture resin is counterproductive for treatment of a high chloride water.
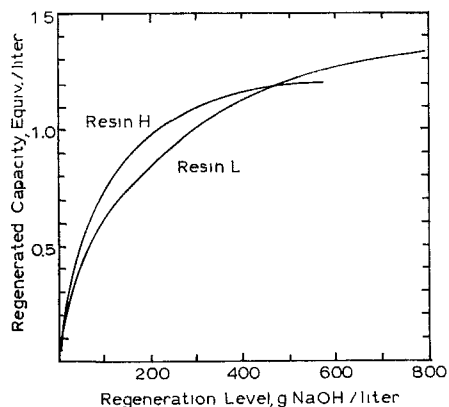


Fig. 6. Estimated regeneration curves for two type I resins.

## LIMITATIONS

For an elution curve to follow eqn. 2, the separation factor must be constant across the exchange. In exchanges between monovalent ions, the separation factor, $\alpha_{AB}$, and selectivity coefficient, $K_{AB}$ are identical. The dependence of $K_{AB}$ on resin composition, $\bar{x}_A$, has been reported for a large number of systems. Fortunately, in the majority of these cases the change of $K_{AB}$ with $\bar{x}_A$ is small. An average value can be used to give a regeneration curve of sufficient accuracy for estimation purposes.

The most notable exceptions occur in anion exchanges in which one of the ions has a high dipole. Gregor et al.[7] have shown this for chlorate, thiocyanate and chloroacetate. Fig. 7 shows the displacement of chloride by bicarbonate ion (1.0 $N$ $NaHCO_3$) on a Type I resin. The failure of the data to fit more closely a curve generated by eqn. 3 is probably due to a change in $\alpha_{HCO_3, Cl}$ across the exchange. The same is true for the fit in Fig. 4.



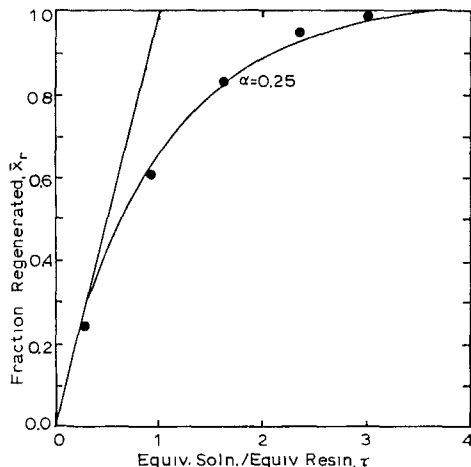Fig. 7. Elution of $Cl^-$ with $HCO_3^-$ from type I resin.

In exchanges between monovalent ions and multivalent ions the separation factor and the molar selectivity coefficient are not equivalent. In fact, if the molar selectivity coefficient is reasonably constant across the exchange, it is impossible for the separation factor to be constant. Therefore, elutions between monovalent and divalent ions do not fit the family of curves generated by eqn. 2. Further, variations in the value of the molar selectivity coefficient of two orders of magnitude have been observed across exchanges between divalent anions and hydroxide ion.

As with any method of approximation, care must be taken that the system involved behaves in the expected manner. While estimates of regeneration curves from selectivity data are invaluable for preliminary process evaluation, they must be confirmed by laboratory data once the process is to be implemented.

ACKNOWLEDGEMENT

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