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## ION EXCHANGE IN AGITATED BEDS

### SIMULATION OF AN ION-EXCHANGE COLUMN BY A MODEL OF AGITATED TANKS IN CASCADE

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#### SUMMARY

Ion exchange in a stirred reactor is considered in terms of the influence of the non-linearity of the equilibrium isotherm on the outlet concentration. This study is supported by experimental results for the  $\text{Cl}^-$ - $\text{OH}^-$  exchange accompanied by neutralization.

An iteration method is presented for calculation of the state of the column in the cyclic mode. For this, the column is simulated by a "tanks-in-series model" and two concepts are considered: (1) width of the mass transfer and (2) saturation factor and regeneration factor.

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#### INTRODUCTION

For calculations on ion-exchange columns, it is important to know the breakthrough curves. The prediction of such curves (histories of concentration) is an important step in the calculation. The earliest model is the "theoretical plate model" of Martin and Synge<sup>1</sup>, developed in 1941, but this model fails in the prediction of zone dispersion as a function of the different variables (flow-rate, particle size, etc.). Furthermore, the equilibrium isotherm is linear in the Martin and Synge work.

The "tanks-in-series model", used in chemical reactor theory<sup>2</sup>, is equivalent to the plate model. The utilization of the tanks-in-series model is advantageous because the separation of the contribution of the zone spreading from the axial dispersion, film diffusion, etc., is possible.

In the case of ion-exchange operation, the most important parameter is the useful capacity of the column in the cyclic mode, because the saturation and regeneration steps are not completed. In this situation the Martin and Synge approach is not suitable. In our work, we assume that the equilibrium isotherm is, in general, non-linear.

In the first part of this paper we discuss the elementary cell of the model, the stirred reactor, particularly for the case of ion exchange accompanied by neutralization. In the second part, an iteration method is presented for the calculation of any state of the column, such as the cyclic mode of operation. The major assumption is the instantaneous establishment of equilibrium at the solid-liquid interface. This means that the axial dispersion, measured by  $N$  (number of cells), is the controlling mechanism of the operation ( $N = \text{Peclet number}/2$ ).

THEORETICAL STUDY OF ION EXCHANGE IN AN AGITATED BED

We consider a stirred reactor that contains two phases: the solid phase (resin) and the liquid phase (solution). The material balance can be written in the form

$$Uc_0 = Uc_1 + V_S \cdot \frac{dc_1}{dt} + V_R \cdot \frac{dq}{dt} \tag{1}$$

We assume that the equilibrium isotherm is of the "law of mass action" type,  $q = f(c)$ , with

$$K = \frac{q(c_0 - c_1)}{(Q - q)c_1} \tag{2}$$

By introducing the dimensionless variables

$$\tau = \frac{V_S}{U}$$

$$\frac{1 - \varepsilon}{\varepsilon} = \frac{V_R}{V_S}$$

$$F = \frac{c_1}{c_0}$$

and

$$\theta^* = \frac{t}{t_{ST}}$$

the system of eqns. 1 and 2 can be reduced to the equation

$$\frac{dF}{d\theta^*} = \frac{1 - F}{g(F)} \tag{3}$$

An analysis of the influence of different factors ( $\varepsilon$ ,  $c_0$  and  $K$ ) is possible after integration (numerical or analytical)<sup>3</sup> of eqn. 3.

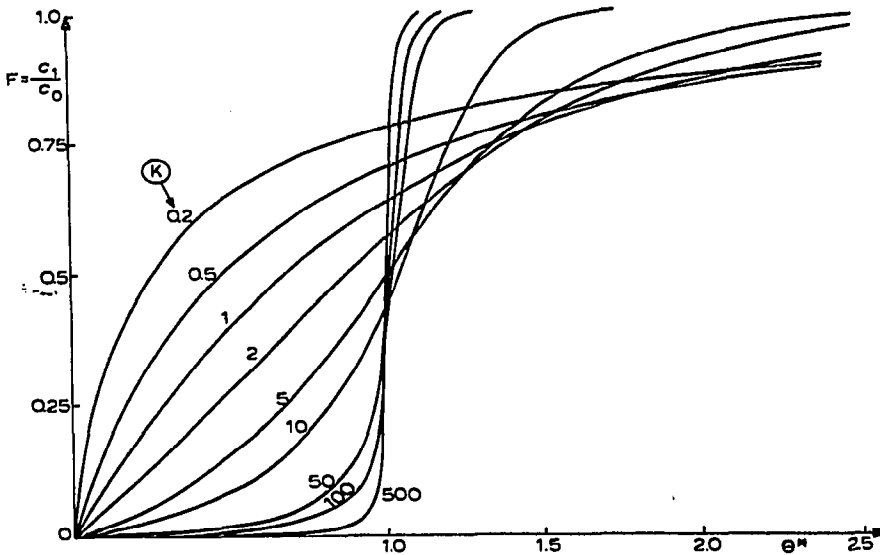


Fig. 1. Influence of  $K$  on the response of a stirred reactor.  $\varepsilon = 0.4$ ;  $Q = 1.4 N$ ;  $c_0 = 0.05 N$ .

Fig. 1 shows the calculated results for a stirred reactor; the response of the system to a step change in the concentration at the entry is mainly dependent on  $K$  ( $K$  characterizes the non-linearity of the isotherm).

#### EXPERIMENTAL RESULTS FOR ANION EXCHANGE IN A STIRRED REACTOR

We have used the anionic resin Duolite a102 D produced by Diaprosim (Chauny, France) in the  $\text{ROH}^-$  form. The solution passed through the reactor was  $\text{HCl}$ ; the exchange between  $\text{Cl}^-$  and  $\text{OH}^-$  ions is accompanied by neutralization and the equilibrium becomes irreversible.

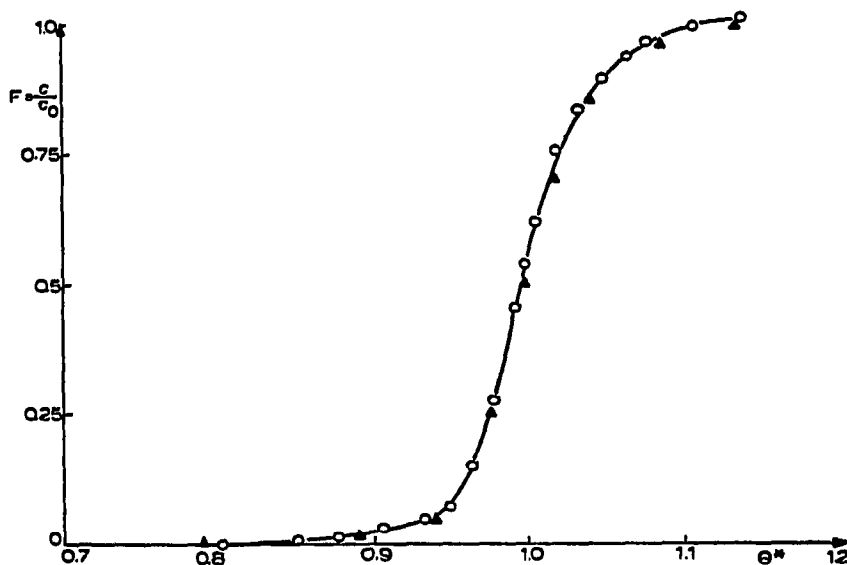


Fig. 2. Calculated (▲) and experimental (○) results.  $V_{\text{reactor}} = 79$  ml;  $V_R = 21$  ml;  $c_0 = 0.01$  N; flow-rate = 13.44 ml/min.;  $t_{ST} = 205.4$  min.

Fig. 2 represents experimental and calculated (for  $K = 500$ ) results for different conditions. Apparently the hypothesis of instantaneous equilibrium is valid under the conditions of the present work.

#### SIMULATION OF AN ION-EXCHANGE COLUMN BY THE TANKS-IN-SERIES MODEL

We assume that the column is divided into a series of reactors; for reactor  $i$ , we can write

$$\frac{dF_i}{d\theta^*} = \frac{F_{i-1} - F_i}{f(F_i)} \quad (4)$$

Some numerical results of the integration of eqn. 4 by the fourth order Runge-Kutta method (the boundary conditions are: (1) at any time  $c = c_0$  at the entry of the column and (2) at  $t = 0$  the concentrations  $c$  and  $q$  are zero in the column) are shown in Figs. 3 and 4 (dispersive and stable fronts).

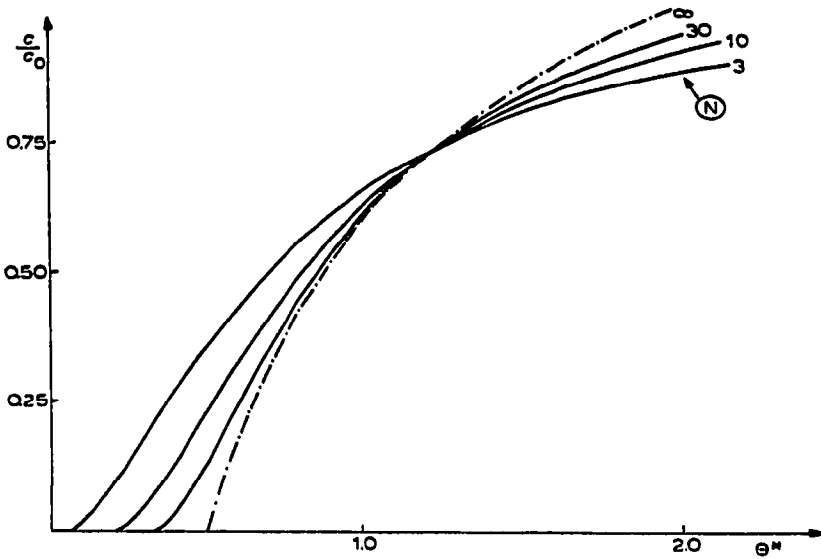


Fig. 3. Influence of  $N$  on the response of an anion-exchange column (tanks-in-series model) for  $K = 0.5$ .  $c_0 = 0.05 N$ ;  $Q = 1.4 N$ ;  $\epsilon = 0.4 N$ . Broken line: equilibrium theory in absence of axial dispersion:  $c/c_0 = (\sqrt{r/T} - r)/(1 - r)$ .

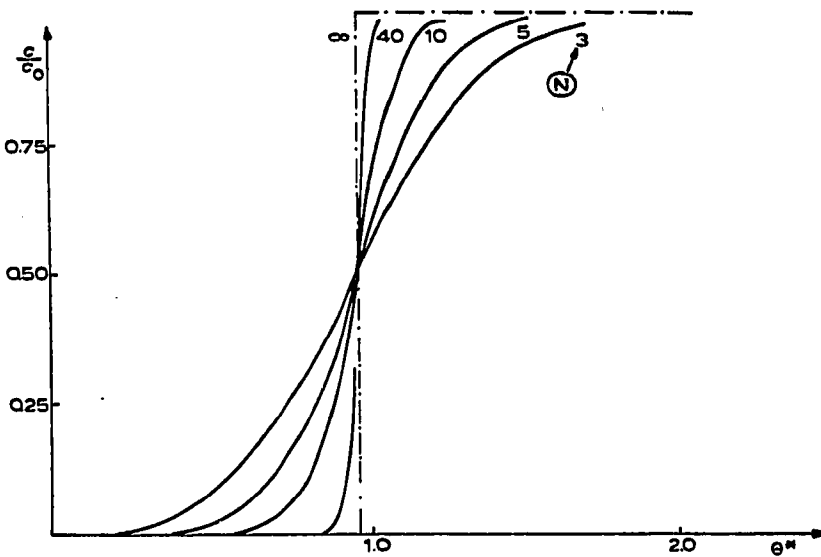


Fig. 4. Influence of  $N$  on the response of an anion-exchange column (tanks-in-series model) for  $K = 2$ .  $c_0 = 0.05 N$ ;  $Q = 1.4 N$ ;  $\epsilon = 0.4 N$ . Broken line: equilibrium theory in absence of axial dispersion:  $c/c_0 = H(\theta^* - 1)$ , where  $H =$  Heaviside function.

For a breakthrough curve, we can define the "width of the mass transfer zone",  $Z_E$  (ref. 4), by

$$Z_E = L (\theta_S^* - \theta_E^*) \tag{5}$$

and obtain a relationship, for each  $K$ , between  $N$  and  $Z_E/L$ :

$$N = a \left( \frac{Z_E}{L} \right)^b \tag{6}$$




Now, for each step (saturation ( $S$ ) or regeneration ( $R$ ) of the column) we can calculate the saturation factor,  $F_S$ , and the regeneration factor,  $F_R$ , (ref. 5), respectively, defined by

$$F_{S \text{ (or } R)} = \int_0^{\theta^*} (1 - F_{1S \text{ (or } R)}) d\theta^*$$

and plot the curves  $F_S = \varphi_1(\theta^*)$  and  $F_R = \varphi_2(\theta^*)$ . We assume that the shape of the saturation (or regeneration) front is independent of the regeneration (or saturation) level.

Next we can calculate the state of the column. We start with a completely regenerated column ( $F_R = 0$ ,  $F_S = 1$ , in each "state"  $F_{Ri} + F_{Si} = 1$ ); after partial saturation of the column we know the "available capacity of the resin",  $Q_0$  (so  $t_{ST}^0$ ) and by means of eqns. 5 and 6 we obtain  $N_0$ . From the plot  $F_S = \varphi_1(\theta^*)$  we obtain  $F_{S1}$ . The iteration method is presented in Table I.

TABLE I  
ITERATION METHOD OF CALCULATION

State of the column	Parameters $F_R$ $F_S$	Steps of calculation
Initial		
At the end of saturation 1		$t_{ST_0} = \tau \frac{Q_0}{\epsilon c_0} \rightarrow \left( \frac{Z_E}{L} \right)_0 \rightarrow N_0 \rightarrow F_{S1}$
At the end of regeneration 2		$t_{ST_1} = \tau \frac{Q_1}{\epsilon c_0} \rightarrow \left( \frac{Z_E}{L} \right)_1 \rightarrow N_1 \rightarrow F_{R2}$
At the end of saturation 3		$t_{ST_2} = \tau \frac{Q_2}{\epsilon c_0} \rightarrow \left( \frac{Z_E}{L} \right)_2 \rightarrow N_2 \rightarrow F_{S2}$

CONCLUSIONS

The ion-exchange operation in stirred reactors is of interest when the solid-liquid isotherm is favourable. In such a situation the performance is similar to that of a fixed bed, leading to a simpler design. The simulation technique of an ion-exchange column by the "tanks-in-series model" is the basis of the iterative calculation of a column "state"; for this purpose, it is necessary to determine the experimental saturation (and regeneration) fronts in a completely regenerated (or saturated) column.

SYMBOLS

$c_0, c_1$  solution concentrations at the entry and the exit of the reactor (mequiv./ml)  
 $L$  column length (cm)

$q$	concentration in the resin (mequiv./ml).
$Q$	capacity of the resin (mequiv./ml).
$t_{ST}$	stoichiometric time (sec); $t_{ST} = [\varepsilon c_0 + (1 - \varepsilon)Q]\tau/\varepsilon c_0$ .
$U$	flow-rate of solution (ml/sec).
$V_R, V_S$	volumes occupied by the solid and liquid phases, respectively (ml).
$\theta_{S \text{ (or } E)}^*$	stoichiometric time at $c = 0.95c_0$ (or $c = 0.05c_0$ ).

## REFERENCES

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