Greek Letters

δ_i = dimensionless reservoir volumes, V_iH/AL
λ_n = roots of $\tan \lambda_n = -(\delta_1 + \delta_2)\lambda_n/(1 - \delta_1\delta_2\lambda_n^2)$

LITERATURE CITED

Reible, D. D., and F. H. Shair, "A technique for the measurement of gaseous diffusion in porous media," *J. of Soil Sci.*, **6**, (1982).

Shair, F. H., and D. S. Cohen, "Transient ordinary and forced diffusion in a tube connecting stirred-tank end bulbs of finite size," *Chem. Eng. Sci.*, **24**, p. 39 (1869).

Soles, E., J. M. Smith, and . R. Parrish, "Gas transport through polyethylene membranes," *AIChE J.*, **28**, 3, p. 474 (1982).

Spacek, P., and M. Kubin, "Diffusion in Gels," *J. of Polym. Sci.*, Part C, **16**, p. 705)1967.

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Mathematical Modelling of the Ligand Exchange Process

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INTRODUCTION

Ligand exchange is a process in which a substance is removed from solution by complexing with a metal ion held on an ion exchange resin. For example, ammonia can be removed from water solution by complexing with Cu(II) ion held on a cation exchange resin. The term, ligand exchange, was coined by Helfferich (1962a,b,c) who studied the process extensively. The process has potential applications in pollution control. Where applicable it can reduce the concentration of a pollutant to a very low level. Because of the specificity of complex formation it offers the possibility of selectively removing specific pollutants. Dawson (1964) and Dobbs (1975, 1976) developed a process for removing ammonia from water by complexing with Cu(II) ion held on a hydrous zirconium oxide ion exchanger. Jeffrey (1977), in this laboratory, studied various metal ion-organic resin combinations for ammonia removal. Of the systems studied the Cu(II)-carboxylic acid type resin combination gave the best results.

The objective of this paper is to apply an ion-exchange-type mathematical model to ligand exchange conducted in a fixed bed of resin. It will be seen that the model gives a good fit to experimental data using plausible values of model parameters.

THE MODEL

Ligand exchange is mathematically analogous to adsorption or ion exchange with a highly nonlinear equilibrium curve. For this reason the Thomas model (Thomas, 1944) for fixed-bed ion exchange on a bed of granular solid was chosen. A material balance on the fluid phase in the bed gives

$$\epsilon \frac{\partial c}{\partial t} + \rho_B \frac{\partial q}{\partial t} + \epsilon v \frac{\partial c}{\partial x} = 0 \tag{1}$$

The Thomas model uses a chemical reaction type expression for the adsorption rate at a point in the bed,

$$\rho_B \frac{\partial q}{\partial t} = ka\left[c\left(1 - \frac{q}{q_m}\right) - \frac{1}{K}(C_o - c)\frac{q}{q_m}\right] \tag{2}$$

where k is a kinetic rate constant and K is the adsorption equilibrium constant. The rate expression of Eq. 2 is consistent with an equilibrium relation of Langmuir type,

$$\frac{q}{q_m} = \frac{K(c/C_o)}{1 + (K-1)c/C_o} \tag{3}$$

The Cu(II)-NH$_3$ system considered here forms labile complexes-the coordinated ammonia exchanges rapidly with other ligands. It is reasonable therefore to treat the exchange rate as mass transfer controlled. An effective value of the rate constant was calculated as described by Sherwood, Pigford and Wilke (Sherwood et. al., 1975). This procedure involves adding mass transfer resistances for the fluid phase and the resin phase, then correcting for the effect of the nonlinear equilibrium curve.

$$\frac{1}{k} = \frac{1}{b}\left[\frac{1}{k_f} + \frac{C_o}{k_p q_m \rho_B}\right] \tag{4}$$

The correction factor b was obtained from a graph given by Sherwood et al. (1975). The Thomas solution takes the form

$$\frac{c}{C_o} = \frac{J(n/K,nT)}{J(n/K,nT) + [1 - J(n,nT/K)]\exp[(1 - K^{-1})(n - nT)]} \tag{5}$$

with

$$n = \frac{kax}{v\epsilon} \tag{6}$$

and

$$T = \frac{v\epsilon C_o t}{q_m \rho_B X} \tag{7}$$

for the range of parameters in this paper the functions $J(n/K,nT)$ and $J(n, nT/K)$ reduce to 1.0 and 0.0 respectively so the solution is

$$\frac{c}{C_o} = \frac{1}{1 + \exp[(1 - K^{-1})(n - nT)]} \tag{8}$$

TABLE 1. EXPERIMENTAL CONDITIONS

	Run II	Run III
Column Inside dia., cm	0.873	0.873
Feed Rate, cm^3/s	0.01201	0.02402
NH_3 Content of Feed, M	0.2188	0.0823
Bed Volume, cm^3	7.91	8.26
Resin Pellet Dia., cm	0.06	0.06
Resin Capacity, mol NH_3/cm^3 Bed	0.003252	0.002344
Bed Void Fraction	0.355	0.355

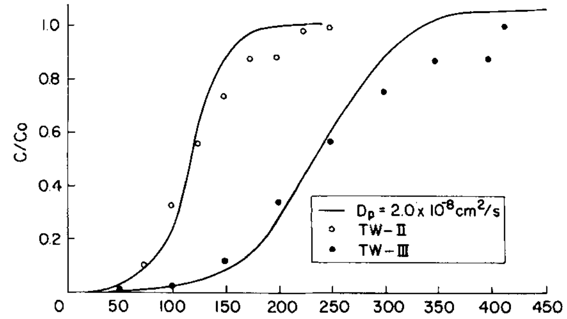

Figure 1. Breakthrough curves for ammonia exchange.

EXPERIMENTAL DATA

Breakthrough curves were obtained for a laboratory bench scale ligand exchange column treating NH_4OH solution with Cu(II). Table 1 shows the experimental conditions.

Resin was Amberlite IRC-50 carboxylic acid type cation exchange resin loaded with Cu(II).

Figure 1 shows the experimental points. The lines were calculated from the mathematical model.

APPLICATION OF THE MODEL TO THE DATA

The equilibrium curve for the NH_3-Cu(II) system was calculated by the method described by Helfferich (1962a) and then modified to agree with the column capacity determined experimentally. The equilibrium relation given by Helfferich is based on the formation constants for the complexes formed by ammonia with copper.

$$\frac{\overline{M}_A}{m_A} = 1 + \frac{\overline{M}m[K_1 + K_2m_A + 3K_3m_A^2]}{[1 + K_1m_A + K_2m_A^2 + K_3m_A^3]} \tag{9}$$

In this equation m_A is the molality of ammonia in the liquid phase in solution, while $\overline{M}_A$ is the molality of the ammonia in the resin phase. Jeffrey found that at saturation the resin contains approximately three moles of ammonia per atom of copper. The equation accordingly includes formation constants, K_1, K_2 and K_3, for complexes with one, two and three molecules of ammonia. The formation constants in the resin phase were assumed equal to those determined at 298 K in ordinary aqueous solution (Yatsimirskii et al., 1966), $K_1 = 1.408 \times 10^4$, $K_2 = 4.46 \times 10^7$, $K_3 = 3.46 \times 10^{10}$.

The resulting equilibrium curve is shown in dimensionless form in Figure 2 as the solid line. This curve was now approximated by a Langmuir isotherm, dotted line, using $K = 200$. The approximating curve was chosen for greatest accuracy in the range $c/C_o = 0.5$ and above.

The breakthrough curve for Run II was used to obtain the value of the reaction rate parameter k for this run. The line for run II on Figure 1 is based on $k = 1.55 \times 10^{-4}$ cm/s. Now the value of the corresponding resin-phase diffusivity was calculated by Eq. 4. The fluid-phase mass transfer coefficient was obtained from the j factor correlation given by Sherwood et al. (1975) for packed beds. The resin phase mass transfer coefficient was related to the diffusivity by the equation

$$k_p = \frac{10D_p}{d_p(1 - \epsilon)} \tag{10}$$

from the same source. This gave a resin-phase diffusivity of 2.0×10^{-8} cm^2/s.

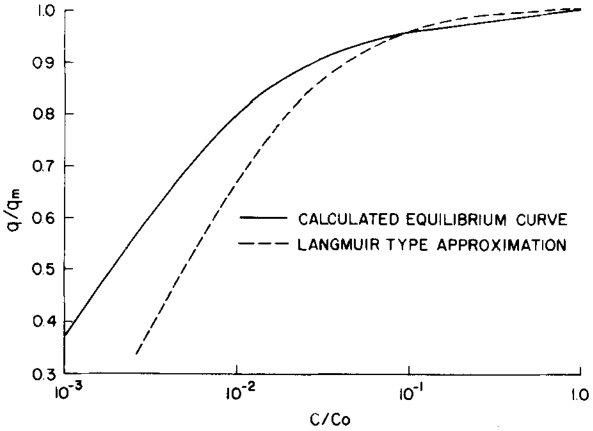

Figure 2. Equilibrium curve for NH_3-Cu(II)-carboxylic acid resin.

TABLE 2. MODEL PARAMETERS

	Run I	Run II
Co, mol/cm^3	0.0002188	0.0000823
q_m, mol/g	0.01005	0.00724
Feed Rate, cm^3/s	0.01201	0.024202
k_f, cm/s	0.00286	0.00390
b	2.05	2.1
k, cm/s	1.55×10^{-4}	2.98×10^{-4}
D_p, cm^2/s	2.0×10^{-8}	2.0×10^{-8}

The resin-phase diffusivity was now used in the model to predict the breakthrough curve for Run III. Figure 1 shows that the predicted curve agrees well with the data. Table 2 gives the model parameters.

The calculated resin phase diffusivity appears small for diffusion into an ion exchange resin. A typical liquid diffusivity is of the order of 10^{-5} cm^2/s which might be reduced to 10^{-6} cm^2/s for ammonia diffusing into the resin matrix. The observed value can be explained as an effective diffusivity for the system studied here. The unsteady state diffusion equation for the ammonia diffusing into the ligand exchange pellet is

$$\epsilon_p \frac{\partial c}{\partial t} + \rho_p \frac{\partial q}{\partial t} = D_e \nabla^2 c \tag{11}$$

where D_e ($\sim 10^{-6}$ cm^2/s) is the diffusivity for the ammonia in the resin. On the lefthand side we have included accumulation terms for the liquid in the resin pores ($\partial c/\partial t$) as well as in the stationary adsorbed phase ($\partial q/\partial t$). Now suppose, for simplicity, that the adsorption equilibrium curve is a straight line and that the liquid phase in the resin is everywhere in equilibrium with the adsorbed phase. Then

$$q = K_e c \tag{12}$$

and

$$\frac{\partial c}{\partial t} = \frac{D_e}{\epsilon_p + \rho_p K_e} \nabla^2 c \tag{13}$$

The effective diffusivity in the resin phase is

$$D_p = \frac{D_e}{\epsilon_p + \rho_p K_e} \tag{14}$$

For the ammonia -Cu(II) system the equilibrium curve is highly nonlinear. If it is represented by a straight line of the form of Eq. 12, the equilibrium constant, K_e, is of the order of 100. The experimental D_p lies therefore in the expected range.

CONCLUSIONS

The Thomas model for fixed bed adsorption successfully correlates experimental data for the NH_3-Cu(II)-carboxylic acid resin ligand exchange system. Mass transfer parameters in the model lie in the expected ranges. The resin phase diffusivity calculated from one experimental run was used successfully to predict the breakthrough curve for a second run with different feed rate and feed concentration. The model should be useful for design and operation of ligand exchange columns.

NOTATION

a = surface area of resin pellets per unit volume of bed, cm^2/cm^3
b = correction factor for nonlinear equilibrium line
c = concentration of NH_3 in liquid phase, mol/cm^3
C_o = feed concentration, mol/cm^3
D_p = resin phase effective diffusivity, cm^2/s
D_e = ammonia diffusivity in resin pores
k = reaction rate constant
k_f = liquid phase mass transfer coefficient, cm/s
k_p = resin phase mass transfer coefficient, cm/s
K = equilibrium constant in Langmuir type isotherm
K_1,K_2,K_3 = formation constants for Cu(II)–NH_3 complexes
m liquid phase molality, mol/kg water
M resin phase molality, mol/kg water
n dimensionless bed length
q concentration of NH_3 in resin phase, mol/g
q_m = resin phase concentration in equilibrium with feed, mol/g
t = time, s
T = dimensionless time
v = velocity of fluid in void spaces of bed, cm/s
$v\epsilon$ = superficial velocity of fluid, cm/s
x = distance from bed inlet, cm
ϵ = void fraction for bed
ϵ_p = pellet void fraction
ρ_B = resin bulk density, g/cm^3
ρ_p = pellet density

LITERATURE CITED

Dawson, G. W., "Process for Removal of Ammonia from Aqueous Streams," U.S. 3,842,000 (1974).

Dobbs, R. A., S. Uchida, L. M. Smith, and J. M. Cohen, "Ammonia Removal from Waste Water by Liquid Exchange," *AIChE Symp. Ser.*, **71**, No. 152, p. 157 (1975).

Dobbs, R. A., "Ligand Exchange Process for Removal of Ammonia," U.S. 3,948,769 (1976).

Helfferich, F., "Ligand Exchange. I: Equilibria," *JACS*, **84**, p. 3237 (1962a).

Helfferich, F., "Ligand Exchange. II: Separation of Ligands Having Different Coordinative Valences," *JACS*, **84**, p. 3242 (1962b).

Helfferich, F., *Ion Exchange*, McGraw-Hill Book Co., New York, p. 222, 445 (1962c).

Jeffrey, M., "Removal of Ammonia from Wastewater Using Ligand Exchange," M.S. Thesis, Louisiana State University (1977).

Sherwood, T. K., R. L. Pigford, and C. R. Wilke, *Mass Transfer*, McGraw-Hill, p. 579, 244 (1975).

Thomas, H. C., "Heterogeneous Ion Exchange in a Flowing System," *JACS*, **66**, p. 1664 (1944).

Yatsimirskii, K. B., and V. P. Vasiliev, *Instability Constants of Complex Compounds*, Van Nostrand, Princeton (1966).

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Hydrodynamic Modelling for Liquid Holdups in Periodically Cycled Plate Columns

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The concept of periodic cycling of liquid and vapor streams in perforated plate columns was developed by Cannon (1961). Solution of the mass transfer equations by McWhirter and Lloyd (1963) showed a theoretical plate efficiency double that of a conventional column. Robertson and Engel (1967) found this efficiency was dependent on the fraction of the liquid holdup drained from the plate. Subsequent extensions to the theory by May and Horn (1968) and Furzer (1973) confirmed these findings.

In all these studies, prior knowledge of the liquid holdups in the column was necessary to solve the mass transfer equations. Horn (1967), Gerster and Scull (1970), and Furzer and Duffy (1976) presented experimentally-based mixing models to overcome this problem. However, no correlations between these models and the design parameters of a column were obtained.

Wade et al. (1969) investigated the liquid and vapor flows in a periodically-cycled column implementing two different sets of tray performance equations. Their simple hydrodynamic model was based on the difference between the wet plate pressure drop and the hydrostatic head, which dictated whether liquid or vapor flow occurred. The other model utilized the more complex analysis of tray behavior by Prince and Chan (1965) with simultaneous liquid and vapor flow.

Larsen and Kummel (1979) further developed the latter model, examining flow profiles in the column. Both groups of workers