Model for Sr-Cs-Ca-Mg-Na Ion-Exchange Equilibria on Chabazite

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Chabazite zeolites are used at Oak Ridge National Laboratory to decontaminate wastewaters containing ^{90}Sr and ^{137}Cs. Treatability studies show that chabazite can remove trace amounts of these nuclides from wastewaters containing much higher concentrations of calcium and magnesium. The design of ion-exchange columns for multicomponent systems requires a method for predicting multicomponent equilibria from binary, ternary and quaternary experiments, since the number of experiments required for an empirical equilibrium model is not generally feasible. Binary interaction parameters for the Wilson equation are used to predict solid-phase activity coefficients for the five-component system. The sum of squares of deviations between experimental and predicted solution concentrations for the data points available is calculated. The average deviation per data point for the five-component system is lower than for some of the ternary- and four-component data sets containing calcium or magnesium.

Introduction

The problem of predicting multicomponent ion-exchange equilibria has attracted the interest of several researchers. Smith and Woodburn (1978) modeled the ternary system chloride-nitrate-sulfate on Amberlite IRA 400 using the Wilson equation. In their approach, an "equilibrium quotient" was defined, which is the selectivity coefficient (also called the relative separation factor) into which the liquid-phase activity coefficients have been factored. Thus, the equilibrium quotient would be the true equilibrium constant for the ion-exchange reaction if the solid-phase activity coefficients were all unity. Smith and Woodburn found statistically best values for the binary interaction parameters of the Wilson equation by fitting equilibrium quotients calculated through the Wilson equation to experimentally based equilibrium quotient data.

Shallcross et al. (1988) followed essentially the same method as Smith and Woodburn in modeling the ternary system calcium-magnesium-sodium on Amberlite 252. The only variation was in the method of calculating liquid-phase activity coefficients. Smith and Woodburn used an extended Debye-Hückel equation, while Shallcross et al. used the Pitzer equation (Pitzer, 1975). Myers and Byington (1985) predicted multicomponent equilibria for the ternary system calcium-magnesium-potassium on KU-1 through an energetic heterogeneity approach, rather than using the Wilson equation. In this study, the data of Robinson et al. (1991) on the strontium-cesium-calcium-magnesium-sodium system were modeled using the Wilson equation for solid-phase activity coefficients, but the Wilson binary interaction parameters were obtained in this study directly from isotherm data rather than fitting equilibrium quotients.

Procedure

For the binary exchange reaction

$$bA^{+a} + a\underline{B}^{+b} \rightleftarrows b\underline{A}^{+a} + aB^{+b}$$

where the underline indicates the species in the solid phase, the equilibrium constant can be expressed in terms of activities:

$$K_{A-B} = \left(\frac{\underline{a}_A}{a_A}\right)^b \left(\frac{a_B}{\underline{a}_B}\right)^a = \frac{(\gamma_A^s y_A)^b (\gamma_B C_B)^a}{(\gamma_A C_A)^b (\gamma_B^s y_B)^a} \tag{1}$$

where

y_i = equivalents fraction of i in the solid phase
C_i = normality of i in liquid phase
γ_i = activity coefficient of i in liquid phase
γ_i^s = activity coefficient of i in solid phase.

The activity coefficients for the cations in the liquid phase can be predicted with confidence using, for example, the Pitzer equations. From experiments, the selectivity coefficients (also called relative separation factors) can be obtained:

$$S_{A-B}=\frac{y_A^b C_B^a}{C_A^b y_B^a} \tag{2}$$

Then, the problem is reduced to extracting solid-phase activity coefficients from the selectivity coefficients and calculated liquid-phase activity coefficients. This must be done within a framework that will allow the prediction of multicomponent solid-phase activity coefficients that are thermodynamically consistent.

Smith and Woodburn calculated solid-phase activity coefficients with the Wilson equation, which satisfies the Gibbs-Duhem equation:

$$\ln \gamma_i^s = 1-\ln\left(\sum_{j=1}^{M} y_j\Lambda_{ij}\right)-\sum_{k=1}^{M}\left(\frac{y_k\Lambda_{ki}}{\sum_{j=1}^{M} y_j\Lambda_{kj}}\right) \tag{3}$$

The Wilson equation is applied to the binary experimental data to obtain values for the "interaction parameters," Λ_{ij} and Λ_{ji}, and then these parameters can be used in the Wilson equation for three, four or more component systems.

To extract the values of the interaction parameters from the binary data, Smith and Woodburn defined an equilibrium quotient, λ_{A-B}:

$$\lambda_{A-B}=\frac{(\gamma_B C_B)^a y_A^b}{(\gamma_A C_A)^b y_B^a} \tag{4}$$

Values for the equilibrium quotient for each experimental point can be calculated from the selectivity coefficients and predicted liquid-phase activity coefficients.

The equilibrium quotient can be expressed in terms of the equilibrium constant:

$$\lambda_{A-B}=K_{A-B}\frac{\gamma_B^{s\,a}}{\gamma_A^{s\,b}} \tag{5}$$

Substitution of the Wilson equation (Eq. 3) into this expression for the equilibrium quotient yields:

$$\begin{aligned}\ln \lambda_{A-B}=\ln K_{A-B}-b\Bigg[1-\ln(y_A+y_B\Lambda_{A-B})-\Bigg(\frac{y_A}{y_A+y_B\Lambda_{A-B}}\\ +\frac{y_B\Lambda_{B-A}}{y_A\Lambda_{B-A}+y_B}\Bigg)\Bigg]+a\Bigg[1-\ln(y_A\Lambda_{B-A}+y_B)\\ -\Bigg(\frac{y_A\Lambda_{A-B}}{y_A+y_B\Lambda_{A-B}}+\frac{y_B}{y_A\Lambda_{B-A}+y_B}\Bigg)\Bigg]\end{aligned} \tag{6}$$

This equation contains three unknowns: K_{A-B} and the two interaction parameters. A minimum of three data points are needed to evaluate them. When more than three data points are available, a search procedure can be used to find the set of values of K_{A-B}, Λ_{A-B}, and Λ_{B-A} that minimize the sum of the squares of the deviations between experimental equilibrium quotients from Eq. 4 and predicted equilibrium quotients from Eq. 6 for all points. This is the procedure that was followed by Smith and Woodburn and by Shallcross et al.

The Wilson interaction parameters can be obtained more directly by fitting the isotherm data. For the binary isothermal systems, C_A, the solution concentration of A, may be predicted given the experimental values for the total solution concentration C_t (normality) and the equivalents fraction of component A in the solid phase, y_A:

1. Assume trial values for K_{A-B}, Λ_{A-B}, and Λ_{B-A}.
2. Calculate γ_A^s and γ_B^s from the Wilson equation.
3. Assume trial values for the liquid-phase activity coefficients γ_A and γ_B. For the dilute solutions in this work, values ranged from about 0.7 to near unity.
4. Calculate the predicted value of C_A from the equilibrium constant and a mass balance:

$$C_A+C_B=C_t \tag{7}$$

$$C_A=\frac{y_A\gamma_A^s C_B\gamma_B}{K_{A-B}\gamma_A y_B\gamma_B^s} \tag{8}$$

5. Calculate the liquid-phase activity coefficients γ_A and γ_B from the Pitzer equation using the predicted values of C_A and $C_B=C_t-C_A$. Compare these values with those assumed in step 3.
6. Iterate steps 4, 5 and 6 until liquid-phase activity coefficients no longer vary.
7. Repeat the above steps, varying the values of K_{A-B}, Λ_{A-B} and Λ_{B-A}, to minimize the difference between the experimental and predicted values of C_A and C_B.

This procedure is easily extended to systems with more than two components.

Results

The extent of the data published by Robinson et al. for the strontium-cesium-calcium-magnesium-sodium system is summarized in Table 1. Total solution concentrations including all components did not exceed 0.01 N for any of the data sets. All data were taken at 23°C. Equilibrium quotients were calculated for the binary data from Eq. 4. The Pitzer equation for cations was used to calculate liquid-phase activity coefficients. Because the solutions were so dilute, only the first term in the Pitzer equation was significant.

The procedure used by previous investigators to obtain Wilson interaction parameters from equilibrium quotients (searching for values of K_{A-B}, Λ_{A-B}, and Λ_{B-A} which provide values of λ_{A-B} from Eq. 6 which most closely match experimental λ_{A-B}'s from Eq. 4) was not successful for the present system. Experimental values for equilibrium quotients passed through a maximum when plotted against equivalent fraction in the solid phase, as illustrated for cesium-sodium in Figure 1. Values for the interaction parameters that yielded a theoretical curve matching the data points on both sides of the maximum could not be found.

The data used by Smith and Woodburn contained no solid-phase equivalent fractions below 0.2. Equilibrium quotients from their data decreased monotonically as solid-phase equivalents fraction increased. Similarly, the equilibrium quotients of Shallcross et al. did not exhibit a maximum.

Using the procedure of finding best values for the model

Table 1. Extent of Experimental Data*

No. of Components	Components	No. of Solution/Sorbent Ratios
2	Strontium-Sodium	8
	Cesium-Sodium	6
	Calcium-Sodium	6
	Magnesium-Sodium	7
3	Strontium-Cesium-Sodium	7
	Calcium-Magnesium-Sodium	7
4	Strontium-Calcium-Magnesium-Sodium	6
	Cesium-Calcium-Magnesium-Sodium	6
5	Strontium-Cesium-Calcium-Magnesium-Sodium	13

*From Robinson et al. (1991).

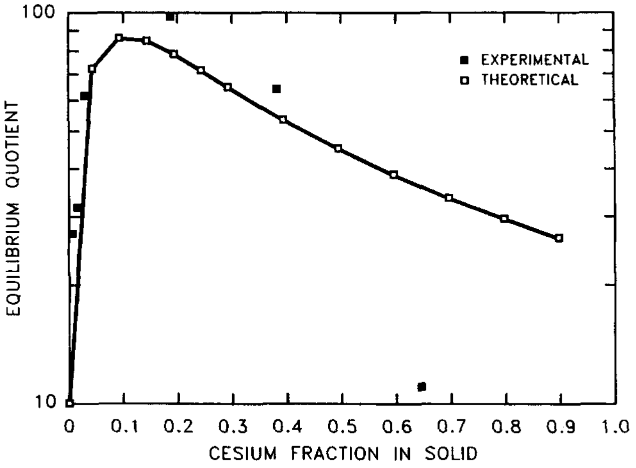

Figure 1. Cesium-sodium equilibrium quotients.

Theoretical points calculated using $K=51$, $\Lambda_{Cs-Na}=0.01$, $\Lambda_{Na-Cs}=3.95$.

parameters directly from the isotherm data, the values for the binary data available were obtained and are given in Figures 2 and 3. The sum of the squares of the deviations between experimental and predicted points were used as a criterion for "best" fit:

$$R=\sum_{i=1}^{N}\left(\frac{C_{A_{exp}}-C_{A_{pred}}}{C_{A_{exp}}}\right)^2 \qquad (9)$$

For comparison of goodness-of-fit between data sets, the R value was divided by the number of data points, N, to obtain a measure related to the average deviation per data point.

Since binary data for strontium-cesium were not available, values for strontium-cesium interaction parameters were obtained by fitting the ternary system strontium-cesium-sodium, using the previously obtained parameter values for strontium-sodium and cesium-sodium. Similarly, values for calcium-magnesium interaction parameters were obtained by fitting the calcium-magnesium-sodium data. Interaction parameters for strontium-calcium, strontium-magnesium, cesium-calcium, and cesium-magnesium were obtained by fitting the four-component data using previously obtained parameter values. The results are summarized in Table 2. No independent values of K_{A-B} were used for the last six component pairs in Table 2, because they can be calculated from the first four and should be consistent with them. For the ternary systems, there are two independent component concentrations to be used in calculating the residual with Eq. 9; for the quaternary systems, there are three independent concentrations. The number of experimental data points N in Table 2 for the last six pairs is greater, in consequence, than the number of solution/sorbent ratios in Table 1.

The set of parameter values in Table 2 was used to predict the five-component equilibrium points for which experimental data were given by Robinson et al. The results are shown in Table 3. Equilibrium liquid-phase concentrations were calculated for strontium, cesium, calcium, and magnesium at 13

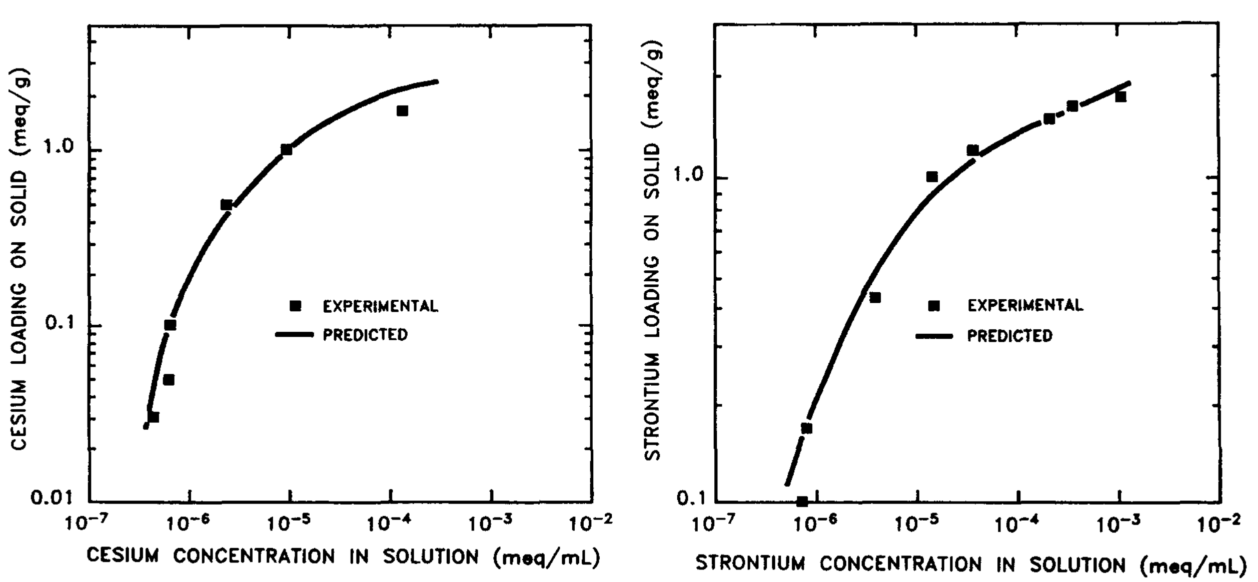

Figure 2. Strontium-sodium and cesium-sodium isotherms.

Model-predicted points calculated using parameter values in Table 2.

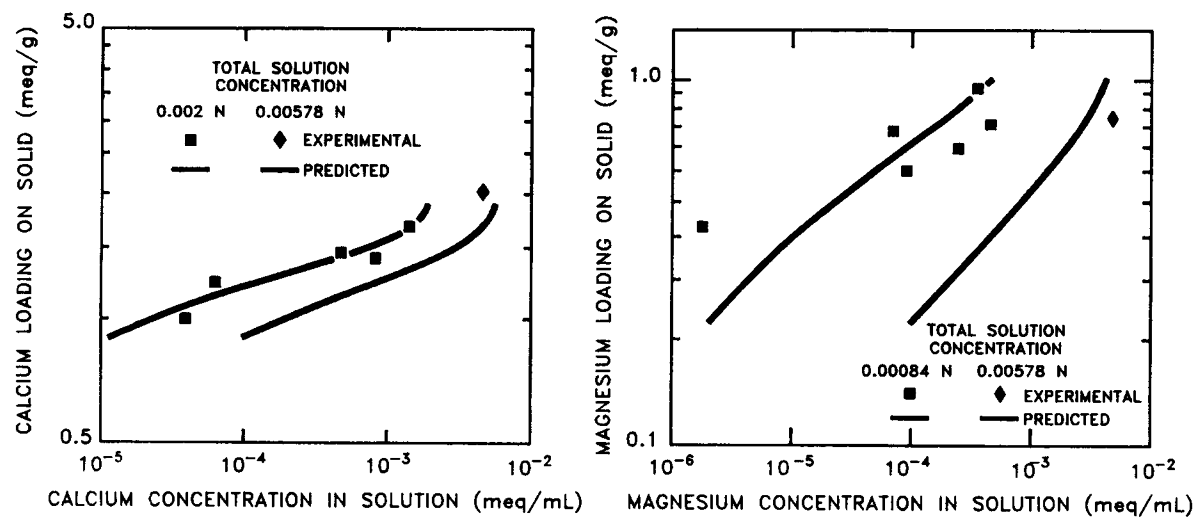

Figure 3. Calcium-sodium and magnesium-sodium isotherms.

Model-predicted points calculated using parameter values in Table 2.

Table 2. Wilson Interaction Parameter Values

Binary Components					Exp. Data	Goodness of
A	B	K_{A-B}	Λ_{A-B}	Λ_{B-A}	Points, N	Fit, R/N
Strontium	Sodium	0.159	7.96	0.112	8	0.13
Cesium	Sodium	51	0.01	3.95	6	0.10
Calcium	Sodium	0.022	86	2.0	6	0.25
Magnesium	Sodium	0.0005	20	4.0	7	5.1
Strontium	Cesium	—	0.001	2.0	14	0.11
Calcium	Magnesium	—	52	92	14	0.40
Strontium	Calcium	—	25	4.0	18	0.65
Strontium	Magnesium	—	0.03	42	18	0.65
Cesium	Calcium	—	4.8	0.2	18	0.22
Cesium	Magnesium	—	2.0	100	18	0.22

concentrations, including two different total solution concentrations. Strontium and cesium concentrations spanned three orders of magnitude. For these 52 predicted concentrations, the R/N was 0.30, which is comparable to or better than some binary, ternary and quaternary data sets including calcium or magnesium, as shown in Table 2.

Application to ORNL Low-Level Wastewater

The equilibrium model will be used in conjunction with a mass-transfer kinetic model for optimized designs of chabazite columns. Typical concentrations in ORNL wastewater are as follows:

Cation	Concentration
Sr^{+2}	1.7×10^{-11} meq/mL
Cs^{+1}	0.9×10^{-12}
Ca^{+2}	2×10^{-3}
Mg^{+2}	6.6×10^{-4}
Na^{+1}	2.0×10^{-4}

Using the model parameters in Table 2 to predict equilibrium concentrations for an application of chabazite of 10 g/L to the wastewater, decontamination factors (DFs) (feed concentration/final concentration) of 1,400 for strontium and 1,600 for cesium are calculated. If sodium is added to the wastewater to a level of 0.1 N, calculated DFs drop to 1.7 for strontium

Table 3. Predicted Liquid Compositions for the Five-Component Data

Liq./Sol. mL/g	*Sr* conc., meq/mL Exp.	*Sr* conc., meq/mL Pred.	*Cs* conc., meq/mL Exp.	*Cs* conc., meq/mL Pred.	*Ca* conc., meq/mL Exp.	*Ca* conc., meq/mL Pred.	*Mg* conc., meq/mL Exp.	*Mg* conc., meq/mL Pred.
Total Dissolved Solids: 5.76 × 10^{-3} meq/mL								
25	1.16E-06	1.39E-06	4.87E-07	4.87E-07	4.99E-07	1.35E-07	4.49E-06	2.35E-06
50	2.39E-06	3.10E-06	8.78E-07	7.51E-07	4.99E-07	3.39E-07	6.34E-06	6.41E-06
99	6.24E-06	8.31E-06	1.82E-06	1.62E-06	4.99E-07	12.3E-07	2.04E-05	2.73E-05
504	6.26E-04	4.60E-04	4.66E-05	7.01E-05	5.75E-04	2.72E-04	7.83E-04	8.69E-04
1,012	1.34E-03	0.80E-03	2.35E-04	1.89E-04	1.31E-03	0.37E-03	8.88E-04	10.4E-04
1,955	1.63E-03	2.28E-03	4.02E-04	5.46E-04	1.58E-03	1.81E-03	9.16E-04	9.93E-04
Total Dissolved Solids: 1.45 × 10^{-3} meq/mL								
50	1.69E-07	0.34E-07	1.07E-07	0.83E-07	3.24E-06	0.38E-08	1.05E-06	0.55E-07
100	2.05E-07	0.83E-07	1.70E-07	1.08E-07	3.24E-06	0.86E-08	8.54E-07	1.35E-07
201	2.58E-07	1.87E-07	2.60E-07	1.69E-07	3.24E-06	0.23E-07	5.38E-07	4.00E-07
506	6.46E-07	7.74E-07	5.98E-07	5.40E-07	3.24E-06	1.48E-07	2.05E-06	3.23E-06
830	2.20E-06	2.74E-06	1.46E-06	1.66E-06	3.24E-06	0.81E-06	1.13E-05	1.79E-05
1,240	1.69E-05	1.22E-05	4.68E-06	5.63E-06	1.94E-05	0.59E-05	9.10E-05	6.37E-05
2,370	1.86E-04	0.60E-04	2.89E-05	2.53E-05	2.11E-04	0.40E-04	2.02E-04	0.83E-04

and 50 for cesium. These decontamination factors are consistent with those observed in practice.

Conclusion

The model was based on equilibrium constants for the ion-exchange reactions written in terms of liquid- and solid-phase activities. Liquid-phase activity coefficients were calculated from the Pitzer equation for cations. Solid-phase activity coefficients were calculated from the Wilson equation. Agreement between experimental and predicted concentrations for the five-component data was better than for some of the ternary- and four-component data. Agreement was best for cesium ($R/N = 0.064$) and strontium ($R/N = 0.17$) and worst for calcium ($R/N = 0.71$). Cesium and strontium concentrations were measured by Robinson et al. using radioactive tracers, and detection limits for these species were more precise by approximately an order of magnitude than for calcium, magnesium, and sodium. This factor probably accounts for the lower average deviations for the cesium and strontium data.

Literature Cited

Myers, A. L., and S. Byington, "Thermodynamics of Ion Exchange: Prediction of Multicomponent Equilibria from Binary Data," *Ion Exchange: Science and Technology*, A. E. Rodrigues, ed., NATO ASI Series E 107, p. 119 (1986).

Pitzer, K. S., and J. J. Kim, "Thermodynamics of Electrolytes: IV. Activity and Osmotic Coefficients for Mixed Electrolytes," *J. Amer. Chem. Soc.*, **96**(18), 5701 (1974).

Robinson, S. M., W. D. Arnold, and C. H. Byers, "Multicomponent Ion Exchange Equilibria in Chabazite Zeolite," *ACS Symp. Ser.*, No. 486, *Emerging Technologies in Hazardous Waste Treatment II*, D. W. Tedder and F. G. Pohland, eds. (1991).

Shallcross, D. C., C. C. Herrmann, and B. J. McCoy, "An Improved Model for the Prediction of Multicomponent Ion Exchange Equilibria," *Chem. Eng. Sci.*, **43**(2), 279 (1988).

Smith, R. P., and E. T. Woodburn, "Prediction of Multicomponent Ion Exchange Equilibria for the Ternary System SO_4^{2-}-NO_3^--Cl from Data of Binary Systems," *AIChE J.*, **24**(4), 577 (1978).

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Errata

In the article titled "Simulation of Carbon Gasification Kinetics Using an Edge Recession Model" by Kyotani et al. (July 1993, p. 1178), the following corrections are made.

- Equation 4 (p. 1181) should read as follows:

$$\text{RSA} = \frac{\text{number of zig-zag} + \text{armchair} + \text{type D sites}}{\text{number of remaining C atoms at given } X} \tag{4}$$

- On p. 1181, first full paragraph, the second sentence should read as follows: "The values listed correspond to reaction probabilities relative to that of singly bonded edge atoms, which is taken to be unity."
- On p. 1184, second column, the reference to the work of Leon y Leon should read: "Leon y Leon, 1993."