THE WILSON EQUATION APPLIED TO THE NON-IDEALITIES OF THE RESIN PHASE OF MULTICOMPONENT ION EXCHANGE EQUILIBRIA

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ABSTRACT

Non-ideal behaviour for liquid and resin phases in an ion exchange system is investigated theoretically and experimentally for the aqueous ternary system K⁺, Na⁺ and H⁺ with Cl⁻. The Pitzer model is applied to the solution non-idealities, and the Wilson approach, based on experimental binary data, is applied to the resin phase. The two models interact through the equilibrium constant, which is calculated using the Gaines and Thomas approach. The predicted ternary data based on the three binary exchange results have been found to be consistent with the experimental results.

INTRODUCTION

To predict multicomponent ion exchange equilibrium, activity coefficient models for both the solution phase and the resin phase are required. It is also desired that the parameters of these models are not influenced by the presence of other ions so that parameters obtained from binary equilibrium data can be used to predict multicomponent equilibria.

In this study a model is presented which uses the Pitzer correlation (1,2) to describe activities in the solution phase. In order to improve the description of the solution phase, new Pitzer parameters were obtained from the original data over the range 0 to 2M instead of those optimised for range 0 to 6M. For the resin phase, the equilibrium constant has been calculated using the approach of Gaines and Thomas (3) see also Argersinger (4) and combined with the Wilson equation to regress the binary interaction parameters from the binary equilibrium data.
MODEL DEVELOPMENT

The system studied may be represented by the following three stoichiometric reactions:

\[ R-\text{H}^+ + \text{Na}^+ \rightarrow R-\text{Na}^+ + \text{H}^+ \] (1)

\[ R-\text{H}^+ + K^+ \rightarrow R-K^+ + H^+ \] (2)

\[ R-\text{Na}^+ + K^+ \rightarrow R-K^+ + \text{Na}^+ \] (3)

where \( R \) denotes the resin.

The equilibrium constants for these equations may be written as:

\[ K_{\text{Na,H}} = \frac{(f_{\text{Na}}y_{\text{Na}})Q_{\text{Na}}}{(f_{\text{H}}y_{\text{H}})Q_{\text{H}}} \frac{(\gamma_{\text{H}}C_{\text{H}})}{(\gamma_{\text{Na}}C_{\text{Na}})} \] (4)

\[ K_{\text{H,K}} = \frac{(f_{\text{H}}y_{\text{H}})Q_{\text{H}}}{(f_{\text{K}}y_{\text{K}})Q_{\text{K}}} \frac{(\gamma_{\text{K}}C_{\text{K}})}{(\gamma_{\text{H}}C_{\text{H}})} \] (5)

\[ K_{\text{K,Na}} = \frac{(f_{\text{K}}y_{\text{K}})Q_{\text{K}}}{(f_{\text{Na}}y_{\text{Na}})Q_{\text{Na}}} \frac{(\gamma_{\text{Na}}C_{\text{Na}})}{(\gamma_{\text{K}}C_{\text{K}})} \] (6)

where \( Q_i \) is the cation exchange capacity in the \( i \) form.

A further constraint involving the resin equivalent ionic mole fraction may also be written:

\[ y_{\text{H}} + y_{\text{Na}} + y_{\text{K}} = 1 \] (7)

Equations 4 to 7 may be used to solve for the composition in the solid phase in equilibrium with a liquid phase at a specified initial composition and concentration. The system is however overspecified because there are four equations and three unknowns. In this case three sets of three equations (4), (5) and (7), (5), (6) and (7), and (4), (6) and (7) are solved to obtain three predicted solid phase compositions, which were then averaged to find a single predicted composition. Variation in the composition predicted by the three sets of equations was within \( \pm 0.01 \).

LIQUID PHASE ACTIVITY COEFFICIENT: PITZER MODEL

The semi-theoretical thermodynamic model proposed by Pitzer (1) to calculate the activity coefficient of an ion in a multicomponent system is used to consider non-idealities in the liquid phase. It has been reviewed and applied by many workers (5,6). The activity coefficient of cation \( M \) present in an aqueous solution of \( c \) cations and \( a \) anions is given by: