Geoderma 151 (2009) 264–269

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

# A Multiresponse method for fitting solid-phase activity coefficient models to ternary ion-exchange data

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ARTICLE INFO

*Article history:*
Received 14 October 2008
Received in revised form 30 March 2009
Accepted 12 April 2009
Available online 12 May 2009

*Keywords:*
Ion-exchange
Multiresponse regression
Vermiculite
Thermodynamics

ABSTRACT

A popular method for fitting solid-phase activity coefficient models in the thermodynamics of ternary ion-exchange has been the Rational method. The standard statistical tests used to compare model functional forms are undefined in the Rational method because all of the dependent variables in the regression (Gibbs Energies) take the value of zero. The present study develops the mathematically equivalent but statistically improved approach of directly fitting Vanselow selectivity coefficients with multiresponse regression. In this multiresponse approach, the Gibbs Energy at equilibrium is set to zero, a selected model is substituted into the equilibrium expression in place of the solid-phase activity coefficients, and the activity coefficient model parameters are optimized numerically until the predicted Vanselow selectivity coefficients are as close as possible to the measured values. This Multiresponse method requires the use of restricted regression to ensure that the equilibrium constants obey the Triangle Rule. An advantage of the Multiresponse method is that it allows for calculation of the coefficient of determination ($R^2$) and $R^2_{\text{adj}}$, which are statistics that can be used to compare solid-phase activity coefficient models. The example solid-phase activity coefficient models compared in this study are the Regular Solution model and a Cox mixture model. When applied to $NH_4^+$–$Ca^{2+}$–$K^+$ exchange on vermiculite, the $R^2_{\text{adj}}$ statistics were found to be 0.944 for the Cox mixture model and 0.826 for the Regular Solution model. These results from the Multiresponse method indicate that the Cox mixture model is superior for this dataset.

## 1. Introduction

The equilibrium condition for an ion-exchange reaction involving a solid exchanger and a liquid is described by the following equilibrium expression (Sposito, 1981):

$$K_{\text{eq}} = \frac{(I\lambda_i)^{Z_j}\left(N_j f_j\right)^{Z_i}}{(N_i f_i)^{Z_j}\left(J\lambda_j\right)^{Z_i}}. \tag{1}$$

Here $K_{\text{eq}}$ is the equilibrium constant, $I$ and $J$ are the concentrations of the two exchangeable ions in the liquid phase, $N_i$ and $N_j$ are the mole fractions of ions $I$ and $J$ in the solid-phase, $Z_i$ and $Z_j$ are the charges on the ions $I$ and $J$, $\lambda_i$ is the liquid-phase activity coefficient, and $f_i$ are the solid-phase activity coefficients. The equilibrium constant depends on the choice of standard state composition, which is the composition where a non-ideal exchanger has an activity coefficient of one (Denbigh, 1963). Rather than the $K_{\text{eq}}$, ion-exchange equilibrium is frequently expressed in terms of the Vanselow selectivity coefficient ($K_{\text{v}}$; Vanselow, 1932) described by Eq. (2).

$$K_{\text{v}} = \frac{(I\lambda_i)^{Z_j}\left(N_j\right)^{Z_i}}{(N_i)^{Z_j}(J\lambda j)^{Z_i}}. \tag{2}$$

$K_{\text{v}}$ can be calculated at individual solid-phase compositions without knowing the solid-phase activity coefficients. The difference between $K_{\text{v}}$ and $K_{\text{eq}}$ is that $K_{\text{v}}$ changes with exchanger composition, unless the exchanger is an ideal exchanger (Sposito and Mattigod, 1979). The $K_{\text{v}}$ can be substituted into Eq. (1) and then rearranged to arrive at Eqs. (3a) and (3b).

$$K_{\text{v}} = K_{\text{eq}} f_i^{Z_j} / f_j^{Z_i} \tag{3a}$$

or

$$0 = \ln K_{\text{v}} - \ln K_{\text{eq}} - Z_j \ln f_i + Z_i \ln f. \tag{3b}$$

Natural waters and waste streams typically have more than two exchangeable ions. There are three reactions and three equilibrium constants in ternary ion-exchange. The equilibrium constants for these three reactions are interrelated through the Triangle Rule given by Eq. (4) (Lowen et al., 1951; Helfferich, 1962). Similar equations can be written for higher order exchange.

$$Z_k \ln K_{\text{eq}\,i/j} + Z_i \ln K_{\text{eq}\,j/k} + Z_j \ln K_{\text{eq}\,k/j} = 0. \tag{4}$$

A number of models are available for estimating both the solid and aqueous-phase activity coefficients (Truesdell 1966; Smith and Woodburn, 1978; Chu and Sposito, 1981; Zemaitis et al., 1986; Pabalan, 1994;

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doi:10.1016/j.geoderma.2009.04.017

Bond, 1995; Snyder and Cavallaro 1997). A large amount of data is available to calculate the aqueous-phase activity coefficients for most ions of interest under the most common concentration ranges (Zemaitis et al., 1986). At the present time, the solid-phase activity coefficient models are less advanced than the aqueous-phase models. For solving solid-phase activity coefficients, a candidate model is typically substituted for the $f_i$ in Eqs. (1), (3a) or (3b), and the candidate model parameters are determined empirically. Many studies have attempted to predict ternary ion-exchange equilibria by assuming that the activity coefficients determined from binary systems are valid in ternary systems (Grant and Sparks, 1989; Bond and Verberg, 1997; Vo and Shallcross, 2005). The method presented in the current study allows for avoidance of this assumption when ternary data is available.

A popular method for empirically determining the activity coefficient model parameters in multi-ion systems is the Rational method of Grant and Sparks (1989). Grant and Sparks (1989) noted that all three exchange reactions (as shown in Eq. (3b)) in ternary ion-exchange can be squared and then summed together to obtain the following relation:

$$0=\sum_{i=1}^{n-1}\sum_{n\geq j\geq i}\left(\ln k_{\mathrm{v},\,i/j}-\ln K_{\mathrm{eq},\,i/j}-z_i\ln f_j+z_j\ln f_i\right)^2. \tag{5}$$

The zero on the left hand side of Eq. (5) is the total Excess Gibbs Energy of the system that is not accounted for by the solid and liquid-phase activity coefficients. Per Grant and Sparks (1989), Eq. (5) is solved by substituting in the numerical value of the $K_{\mathrm{eq}}$, the measured $K_{\mathrm{v}}$ values, as well as a candidate model for each solid-phase activity coefficient. The empirically determined parameters within the solid-phase activity coefficient models are established by varying them iteratively (Kunz, 1957; Vaughan, 2002) until the right side of Eq. (5) is as close as possible to zero (Grant and Sparks, 1989). This method is called the Rational method because it effectively sets the ratio of the activity coefficients equal to the ratio of the Vanselow selectivity coefficient to the equilibrium constant.

The best solid-phase activity model is still being debated, and may not be the same for all systems. Several studies have compared solid-phase activity coefficient models (Grant and Sparks, 1989; Vamos and Hass, 1994; Bond and Verberg, 1997). One of the most effective statistics for comparing models is the coefficient of determination ($R^2$) which provides the proportion of the data variation that is explained by the model (Kleinbaum and Kupper, 1978). The formula for calculating $R^2$ is (Marquardt and Snee, 1974):

$$R^2=1-\left(\frac{\sum_{i=1}^{n} Y_i-\hat{Y}_i}{\sum_{i=1}^{n} Y_i-\bar{Y}_i}\right) \tag{6}$$

where $Y_i$ is the $i$th measured result, $\hat{Y}_i$ is the result predicted by the model for that composition, and $\bar{Y}_i$ is the mean measured result. The reader should note that Eq. (6) is slightly different than the equation commonly reported for $R^2$ by introductory textbooks. Marquardt and Snee (1974) explain that Eq. (6) is the appropriate equation for mixture applications where the independent variables must sum to one.

A limitation with using $R^2$ is that the statistic can always be increased by adding terms to the fitted model, even unjustified terms (Rao, 1971). Consequently, the $R^2{}_{\mathrm{adj}}$ statistic (Eq. (7); Marquardt and Snee, 1974) is often used for comparing models with differing numbers of empirically determined parameters because this statistic is lowered when unjustified terms are included in the model.

$$R^2_{\mathrm{adj}}=1-\left(\frac{\sum_{i=1}^{n} Y_i-\hat{Y}_i/n-p}{\sum_{i=1}^{n} Y_i-\bar{Y}_i/n-1}\right). \tag{7}$$

In Eq. (7), $n$ = the number of data points regressed and $p$ = the number of unconstrained fitted parameters.

There is a limitation to fitting solid-phase activity coefficient models using the Rational method, evident from Eqs. (6) and (7). The $R^2$ and $R^2{}_{\mathrm{adj}}$ statistics are undefined when performing the Rational method because the denominators of Eqs. (6) and (7) would be zero, and it is not possible to divide by zero. They would be zero because the true Excess Gibbs Energy at equilibrium that is unaccounted for by the activity coefficients is always zero theoretically (Denbigh, 1963). Hence, $R^2$ and $R^2{}_{\mathrm{adj}}$ cannot be directly used to compare different solid-phase activity coefficient models when the Rational method is employed.

This limitation will be mitigated in a method presented here to fit solid-phase activity coefficient models to ternary ion-exchange data. This method involves varying the empirically determined parameters in the activity coefficient model until the minimum difference between the measured and predicted $\ln(K_{\mathrm{v}})$ values is obtained. Thus, in the present method, the Vanselow selectivity coefficients are regressed rather than the Gibbs Energy. Each of the following sections describes an aspect of this revised thermodynamic model fitting procedure, here denoted as the Multiresponse method.

## 2. Multiresponse fitting methodology

### 2.1. Test data

An example of data fitting was undertaken to demonstrate the Multiresponse method described in the following sub-sections. The ternary ion-exchange dataset of Evangelou and Lumbarnraja (2002), which has data for $NH_4^+$–$K^+$–$Ca^{2+}$ exchange on the clay mineral vermiculite, was used as the example dataset. The $K_{\mathrm{v}}$ for each data point was calculated using the solid and aqueous-phase concentrations they provided. The aqueous-phase activity coefficients were calculated with the Extended Bromely model (Zemaitis et al., 1986), which has been used previously in ion-exchange thermodynamics studies (Ioannidis et al., 2000). The aqueous-phase concentrations that Evangelou and Lumbarnraja (2002) reported in molarity units were assumed to be the same in the molality units used by the Extended Bromley model. This assumption was verified, to the third significant digit, using water-contents estimated by the method of Reynolds and Carter (2008). The aqueous-phase activity coefficients were found to be effectively independent of composition over the narrow composition range reported by Evangelou and Lumbarnraja (2002). These aqueous-phase activity coefficient values were calculated to be $NH_4^+=0.91$, $K^+=0.91$, and $Ca^{2+}=0.68$. The $\ln(K_{\mathrm{v}})$ data thus calculated are shown in Table 1.

**Table 1**
Vanselow selectivity coefficients calculated for Evangelou and Lumbarnraja (2002) data.

| Sample number | $\ln(K_{\mathrm{v\ NH4/Ca}})$ (kJ/mol) | $\ln(K_{\mathrm{v\ Ca/K}})$ (kJ/mol) | $\ln(K_{\mathrm{v\ K/NH4}})$ (kJ/mol) |
|---|---|---|---|
| 1 | 13.44 | −6.55 | −3.44 |
| 2 | 11.33 | −6.52 | −2.41 |
| 3 | 8.04 | −6.59 | −0.73 |
| 4 | 8.09 | −6.49 | −0.80 |
| 5 | 7.52 | −6.23 | −0.64 |
| 6 | 7.19 | −5.95 | −0.62 |
| 7 | 5.69 | −4.91 | −0.39 |
| 8 | 5.53 | −4.91 | −0.31 |
| 9 | 5.58 | −5.23 | −0.17 |
| 10 | 6.04 | −5.56 | −0.24 |
| 11 | 6.33 | −5.83 | −0.25 |
| 12 | 6.71 | −6.25 | −0.23 |
| Mean | 7.62 | −5.92 | −0.85 |
| Standard deviation | 2.44 | 0.63 | 1.02 |