Modelling Multi-Component Ion Exchange Equilibrium Behaviour

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Abstract

The ability to accurately predict ion exchange equilibria is vital if efficient ion exchange processes and equipment are to be designed. This is particularly true when three or more ionic species are competing with one another for sites on the exchanger. Many models to predict ion exchange equilibrium behaviour have been developed over recent years. The complexity of the models have increased from simple ones which assume ideal behaviour in both phases to ones which can predict behaviour in four-component systems based upon binary equilibrium data. This paper will critically review the models developed in recent years and propose a series of requirements that any proposed ion exchange equilibrium model should meet.

1 Introduction

Ever since the ground-breaking work of Donnan [1] a range of different models have been proposed with varying degrees of accuracy to predict multi-component ion exchange equilibria behaviour. Many of the models developed for multi-component systems have only ever been tested on systems involving just three exchanging ions, i.e., ternary systems. The analytical and numerical challenges demanded of applying the models to higher-order systems are often not addressed by those who propose the models. Moreover, even in simple binary systems involving the exchange of just two ions, some models fail even the most simple of tests, such as ensuring that the equilibrium constant calculated from experimental data is independent of the solution phase concentration. No fully theoretical model has been developed to date that allows equilibrium behaviour to be predicted without at least some experimental data. Much work has been conducted to develop semi-theoretical models that allow multi-component behaviour to be predicted based upon the experimental data of the constitutive binary systems. This paper reviews many of the models developed to predict multi-component ion exchange equilibria and suggests a series of requirements that future ion exchange equilibrium models should meet.

2 Modelling Ion Exchange Equilibria

It has long been recognised that the exchange of two ions between a solution phase and an exchanger or resin phase may be represented by the reversible stoichiometric equation of the type:

$$z_b A^{z_a} + z_a B^{z_b} \rightleftharpoons z_b A^{z_{b*}} + z_a B^{z_a}$$

(1)

where $z_a$ and $z_b$ are the valencies of the ionic species A and B respectively, and the underline denotes that the ion is in the exchanger rather than the solution phase. The equilibrium constant for such an exchange may be written in terms of the activities of the ions in the two phases:
where \( a_i \) and \( a'_i \) are the activities of ionic species \( i \) in the solution and exchanger phases, respectively.

One approach to modelling multi-component ion exchange systems is to predict the system behaviour based upon the experimental data developed for the constitutive binary systems. Thus, when three or more ions are exchanging with one another between the two phases the system is considered to be made up of a number of competing binary equilibria. So, if a system involves the exchange between three ions, A-B-C, it may be represented by the three binary equilibria A-B, A-C and B-C, while a four-component system may be represented by its six constitutive binary systems, A-B, A-C, A-D, B-C, B-D and C-D. It is usually assumed that the equilibrium constant for a binary system involving, say, ionic species A and B, will be independent of the presence of any other ionic species such as C or D.

The equilibrium constant, \( K_{AB} \), is defined in equation (2) in terms of activities rather than concentrations because of the non-ideal behaviour usually exhibited in both the solution and the exchanger phases. The challenge for workers in this area of research relates to the prediction of the activity coefficients in the two phases.

Early workers such as Dranoff and Lapidus[2] and Pieroni and Dranoff[3] assumed that both phases behaved ideally. They made use of the selectivity coefficients, which for a binary system is defined as:

\[
KT_{AB} = \left( \frac{q_A}{C_A} \right)^{\gamma_{AB}} \left( \frac{C_B}{q_B} \right)^{\gamma_{BA}} \tag{3}
\]

where \( q_i \) is the concentration of species \( i \) in the exchanger phase and \( C_i \) is the normality in the liquid phase.

Although the equilibrium constant of an ion exchange process should be a function of temperature only, the selectivity coefficient is also a function of the total concentration and the composition of the solution phase.

Other workers[4,5] developed models to predict the equilibrium behaviour of ternary systems based upon binary system data, assuming that the presence of other counter-ions would not appreciably affect the equilibrium relationships between two particular ions. These workers assumed that the selectivity coefficient values obtained from the data of the constitutive binary systems could be used to predict ternary system behaviour.

In 1975 Elprince and Babcock[6] proposed the use of the Wilson model[7] to estimate the exchanger phase activity coefficients. The Wilson equation applied to the exchanger phase to calculate the activity coefficients is:

\[
\ln y_i = 1 - \ln \left[ \frac{M}{\sum_{j=1}^{M} y_{mi} A_{ij}} \right] - \sum_{k=1}^{M} \left( \frac{y_{mk} A_{ij}}{\sum_{j=1}^{M} y_{mj} A_{ij}} \right) \tag{4}
\]

where \( y_{mi} \) is the mole fraction of component \( i \) in the exchanger phase, \( M \) is the number of counter-ion species in the exchanger phase, and \( A_{ij} \) is the Wilson binary interaction parameter defined such that \( A_{ii} = 1 \) when \( i = j \) and \( A_{ij} > 0 \) when \( i \neq j \). For an ideal exchanger phase, \( A_{ij} = 1 = A_{ji} \) for all \( i \) and \( j \). For a binary system only two parameters, \( A_{AB} \) and \( A_{BA} \) are required to calculate the activity coefficient. Once determined for a binary system these values may be used to calculate the exchanger phase activity coefficients in a multi-component system.

The paper by Elprince and Babcock is also noteworthy as they were the first to suggest the use of Pitzer’s electrolyte solution theory[8] to predict the aqueous phase activity coefficients. While they suggested the use of Pitzer’s model they actually assumed that the solution phase activity coefficients of the two ions in any binary system were equal. The model of Elprince and Babcock was later extended by Wiederfeld and Hossner.[9]

In 1978 Smith and Woodburn[10] proposed the use of the extended Debye-Hückel equation to calculate the activity coefficients in the aqueous solution phase. Like Elprince and Babcock they applied the Wilson model to
estimate the exchanger phase activity coefficients. Using data for the three constitutive binary systems they were able to successfully predict the equilibrium behaviour of the $\text{SO}_4^{2-}$-$\text{NO}_3^-$-$\text{Cl}^-$ ternary system. Other workers have proposed identical models.[11, 12] The model of Smith and Woodburn requires values for three parameters for each constitutive binary system to be known in order that the ternary equilibrium behaviour may be predicted. The parameters are the equilibrium constant, $K_{AB}$, and the two Wilson binary interaction parameters, $\lambda_{AB}$ and $\lambda_{BA}$.

Allen et al.[13] suggested the use of the Hála constraint[14] in an effort to reduce the number of parameters required to adequately characterise the system. In its simplest form when applied to a binary system the Hála constraint is:

$$\lambda_{AB} \lambda_{BA} = 1 \quad (5)$$

When incorporated into the Smith and Woodburn model only two parameters are required to be regressed from the data of each constitutive binary system, namely $K_{AB}$ and $\lambda_{AB}$. Allen et al. applied their modified version of the Smith and Woodburn model to data from other workers. While at first inspection the model appears to adequately fit the data it is disturbing to note that both the equilibrium constants and the Wilson binary interaction parameters are seen to vary significantly with solution concentration. This should not occur and suggests that the model is fundamentally flawed.

In calculating the solution phase activity coefficients the Deybe-Hückel equation does not take into account the effect that the presence of other ions in the system may have on the activity coefficient values. Recognizing this Shallcross et al.[15] proposed a model in which Pitzer's electrolyte solution theory[8] is used to predict the aqueous phase activity coefficients. In all other respects the model was identical to the Smith and Woodburn model. Later Valverde et al.[16] proposed a model identical to that of Shallcross et al. Both the models of [10] and [15] require the three parameters ($K_{AB}$, $\lambda_{AB}$ and $\lambda_{BA}$) for each binary system to be regressed from the binary equilibrium data simultaneously. As the three parameters are highly interdependent the calculated value for $K$ is highly sensitive to slight changes in the values of $\lambda_{AB}$ and $\lambda_{BA}$. Mehablia et al.[17,18] developed an ion exchange equilibrium model in which the equilibrium constant is regressed separately before $\lambda_{AB}$ and $\lambda_{BA}$. By de-coupling these parameters the model yields values for $K$ which are independent of the solution concentration.

Martinez et al.[19] proposed the use of the Meissner and Kusik electrolyte solution theory to calculate the solution phase activity coefficients. While their model was developed for binary ion exchange systems only, de Lucas[20] developed and tested a model for a four-component system which used the Meissner and Kusik model.

The equilibrium model of Ioannidis et al.[21] used the Bromley-Zemaitis model and the Wilson model to calculate the activity coefficients of the solution and exchanger phases respectively. They also developed a method to regress the two Wilson binary interaction parameters from the binary equilibrium data before determining the value for the equilibrium constant.

Nearly all of the preceding models use the Wilson model to predict the activity coefficients in the exchanger phase. Vamos and Haas[22] conducted a study to compare the effectiveness of the Wilson and Margules equations to estimate the exchanger activity coefficients. They concluded that the performance of the Wilson model was slightly better than that of the Margules equation.

A completely different approach to predict multi-component equilibria was adopted by Melis et al.[23] In considering synthetic resin-type exchangers they considered that the resin consisted of two different types of exchange sites, each having its own equilibrium constant for a binary system. The sites were present on the exchanger in equal amounts. They assumed that the solution phase behaved ideally and that all the non-ideal behaviour of the resin phase was accounted for by the use of the two-site model. Later, modified versions of the model were proposed in which the two sites were not assumed to be present in equal numbers.[24, 25]
3 Proposed Tests for Multi-Component Ion Exchange Equilibrium Models

It is proposed that any multi-component ion exchange equilibrium model developed should satisfy a number of criteria. These are listed below:

- Models must be tested for systems involving four exchanging ions, i.e., for quaternary systems.
- $K$ determined for a binary system must be independent of the concentration of the solution phase.
- $K$ determined for a binary system of two exchanging counter-ions must be independent of the ionic species of the non-exchanging co-ion. For example, the $K$ calculated for exchange between Na\(^+\) and Ca\(^{2+}\) ions should be same whether Cl\(^-\), NO\(_3^-\), SO\(_4^{2-}\) or any combination of these ions are present in the system.
- Any parameters regressed from binary equilibrium data, and used to account for non-idealities in the exchanger phase must be independent of the solution phase concentration and the co-ion species. For example, for models in which the Wilson model is used to account for exchanger phase non-idealities, the values of the two interaction parameters, $A_{AB}$ and $A_{BA}$, must be independent of solution concentration.
- Models must be internally-consistent. A number of models end up with more equations to be solved than there are parameters to be determined. The values determined for the parameters should be independent of the particular set of equations used.

References

2) J.S. Dranoff and L. Lapidus, I&EC, 49(8), 1297-1302 (1957).