Use of a Two Parameter Temperature Dependant Semi-Empirical Thermodynamic Ion Exchange Model

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Abstract
A chelating ion exchange resin, Amberlite IRC 748 was investigated for the exchange of copper and sodium from aqueous solutions at three temperatures. A two parameter temperature dependant semi-empirical thermodynamic ion exchange model was used to describe binary systems involving the ions Cu\(^{2+}\) and Na\(^+\). All experiments were conducted with Cl\(^-\) as the non-exchanging anion and at temperatures of 4.0, 20.0 and 40.0 ± 0.1°C. The semi-empirical thermodynamic ion exchange model was shown to predict the shape and position of the ion exchange curves accurately. There was a consistent increase in selectivity of the resin towards copper with an increase in temperature.

Key words: ion exchange, temperature, thermodynamic model

1 Introduction
Chelating ion-exchange resins, such as Amberlite IRC 748, which contain iminodiacetic acid (IDA) functional groups, are known to have a particularly high selectivity for transition metals and so are especially suited to removal of metal ions from multi-metal mixtures. Recently they have been utilized for the treatment of contaminated groundwater from an abandoned landfill site in Antarctica [1]. An important consideration for application of ion exchange technologies in cold regions such as Antarctica is the impact of low temperature on the selectivity of the resin and its ion exchange equilibrium characteristics. In this work a semi-empirical ion exchange model developed by Mumford et al. [2] is applied to the Na-Cu binary exchange system on Amberlite IRC 748. This model incorporates temperature dependence into the semi-empirical thermodynamic ion exchange model through two parameters, the equilibrium constant and the Wilson interaction parameters.

2 Experimental
2.1 Resins and Solutions
The ion exchange media used in the experimental study was Amberlite IRC 748 (Rohm and Haas). The copper chloride and sodium chloride used were of analytical grade (Sigma Aldrich) and MilliQ water was used for all solution preparation. After first washing the resin of any water insoluble residues, the resin was conditioned
into the hydrogen form through consecutive washing with 0.5 mol L\(^{-1}\) hydrochloric acid. It was then transferred into sodium form through washing with a 0.5 mol L\(^{-1}\) sodium hydroxide solution, followed by rinsing with distilled water.

### 2.2 Cation Exchange Capacity

To determine the cation exchange capacity of the sodium form resin, it was contacted with CuCl\(_2\) solution for 72 hours. Tests were conducted by weighing 0.02 g resin into 250 mL flasks. After weighing out the resin, 100 mL of CuCl\(_2\) solution at three concentrations (100, 250 and 500 mg L\(^{-1}\) as Cu) was added to Erlenmeyer flasks and gently agitated at 100 rpm and 20 °C for 72 hours. The copper concentrations in the initial and final solutions were analysed by Atomic Adsorption Spectrophotometry (AAS). The Cu\(^{2+}\) capacity was calculated by plotting the equilibrium concentration of copper on the resin with respect to the equilibrium concentration of the copper in solution. The result was a straight line through the data at constant solid phase concentration which corresponds to the Cu\(^{2+}\) capacity of the resin. When this process was repeated several times, the Cu\(^{2+}\) exchange capacity of the Na form of the resin was found to be 2.69 ± 0.31 mmol g\(^{-1}\) of dry resin.

### 2.3 Batch Equilibrium Experiments

The equilibrium experiments were performed by placing resin of known form and mass into a 250 mL Erlenmeyer flask with precisely 100.0 mL of a CuCl\(_2\) solution and gently agitating for 72 hours. At the conclusion of this period, the solution was separated from the resin, and its concentration determined by AAS. Once the equilibrium composition of the solution phase was determined, the equilibrium composition of the exchanger or resin phase was inferred by use of a simple material balance. For the exchange experiments the initial concentrations of copper in solution were 25, 50, and 100 mg L\(^{-1}\) (0.000775 N, 0.00154 N and 0.00310 N) and the tests were conducted at 4, 20 and 40 °C.

### 2.4 Moisture Tests

For the moisture content, a sample of the resin was weighed and placed in an oven at 105 °C for 24 hours. This process drove off all of the interstitial as well as some of the structural moisture. The resin was then reweighed immediately upon removal from the oven. The moisture content was determined from the difference in mass before and after heating.

### 2.5 Predictive Modeling

The exchanger phase concentration of exchanging ions is linked to the solution phase concentration by the equilibrium model developed by Mehablia [3] and adapted by Mumford et al. [2] to incorporate the effect of temperature. In this technique, the exchange of two ions between a solution phase and an exchanger phase is represented by the stoichiometric equation:

\[
z_b A^{z_a} + z_b B^{z_b} \leftrightarrow z_b A^{z_a} + z_b B^{z_b}
\]

where \(z_a\) and \(z_b\) are the valencies of ionic species \(A\) and \(B\), respectively, and the underline denotes that the ion is in the exchanger phase. The equilibrium constant for such an exchange is written in terms of the activities of the ions.
The solution phase activity coefficients are calculated the Pitzer model [4-6] utilising free ion concentrations as determined by technique proposed by Kester and Pytkowicz [7]. The resin phase activity coefficients are calculated using the Wilson model [8] and the Hála constraint [9]. These models were selected as they are accepted and well characterized for a large variety of ion exchange systems [3]. The thermodynamic equilibrium constant is calculated independently via use of the approach of Gaines and Thomas [10]. Temperature dependence is incorporated through use of the Gibbs Free Energy function. Further information regarding the implementation of this model and the required parameters for this study may all be found in Mumford et al. [2].

3 Results and Discussion

A single set of equilibrium constants and Wilson interaction parameters were regressed at each temperature for the exchanging cation concentrations investigated, presented in Table 1. The natural logarithm of the equilibrium constant and Wilson interaction parameters were then plotted versus the inverse of absolute temperature and a linear relation regressed as shown in Figure 1, and the relation shown in equations (1) and (2). These equations were then utilized to determine the values of the equilibrium constant and interaction parameters which were subsequently used, also presented in Figure 1, to fit the binary ion exchange equilibria.

Table 1: Equilibrium constants and interaction parameters obtained in study

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Equilibrium Constant</th>
<th>Wilson interaction parameter</th>
<th>Equilibrium Constant</th>
<th>Wilson interaction parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>277.15</td>
<td>0.2194</td>
<td>0.7034</td>
<td>0.2258</td>
<td>0.7148</td>
</tr>
<tr>
<td>293.15</td>
<td>0.3320</td>
<td>0.9411</td>
<td>0.3145</td>
<td>0.9124</td>
</tr>
<tr>
<td>313.15</td>
<td>0.4421</td>
<td>1.1779</td>
<td>0.4537</td>
<td>1.1951</td>
</tr>
</tbody>
</table>

\[
\ln(K_{AB}) = -1682.2\left(\frac{1}{T}\right) + 4.5816 \\
\ln(L_{AB}) = -1239\left(\frac{1}{T}\right) + 4.1348
\]

where \(K_{AB}\) is the equilibrium constant, \(L_{AB}\) is the Wilson interaction parameter, \(T\) is the absolute temperature.

The experimental results confirmed a trend of higher selectivity for copper over sodium by Amberlite IRC 748 with a decrease in copper concentration in the aqueous phase, shown in Figure 1, across all temperatures. An increase in temperature also resulted in a higher selectivity for copper, shown through higher equilibrium constants at higher temperatures in Table 1.

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Figure 1: Regression of a) Wilson interaction parameters, b) equilibrium constant, and c) the model predictions at 20°C at various exchanging solution concentrations.

References