THE MODELING OF THE SORPTION OF METALLIC CYANO COMPLEXES ONTO ION EXCHANGE RESINS – RECENT DEVELOPMENTS.

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ABSTRACT

In this work a probabilistic model for the equilibrium sorption onto solid sorbents is presented and it is applied to the sorption of copper and nickel as well as copper and iron onto ion exchange resins. A more negative sorption energy for nickel compared to copper, and copper compared to iron, was observed for the Imac HP555s resin (polystyrene, triethylammonium). In contrast, a more negative sorption energy for copper compared to nickel, and iron compared to copper is observed for the Amberlite IRA 958 resin (polyacrylic, trimethylammonium). These results indicate that the resin structure and hydrophilicity affect the sorption behavior of metal cyanocomplexes. The sorption of copper and nickel onto the two resins studied can be described using only the sorption energy term, while for the copper-iron system other parameters must be considered such as the selectivity factor and the interaction energy. The model parameters have been correlated with results obtained previously using Raman spectroscopy.

INTRODUCTION

The sorption of different species onto a broad range of adsorbents such as soils, activated carbon, biosorbents and ion exchange resins has been studied extensively and applied in the mineral industry. Multi-component sorption systems are found in all fields of the industry and these are the most studied since their complexity challenges the development of models that can be applied to these highly non-ideal systems. Equilibrium sorption in multi-component systems is usually modeled using thermodynamic principles. Based on binary sorption, the behavior of multi-component systems is predicted using the law of mass action to carry out the equilibrium sorption modeling. Non-ideal behaviors are considered through the non-ideal behavior of the resin and the solution as well, taking the Pitzer equations, for instance, to determine the activity of ions in aqueous solutions while the Wilson equation (Meahlia et al., 1996) is used to assess the activities of the species loaded onto the resin phase.

The accuracy of these models relies on the accuracy of the set of equations used to predict the activity coefficient of the species in the aqueous and resin phases. In typical hydrometallurgical systems, where a mixture of cations, anions, ligands, complexes as well as high ionic strengths are the typical conditions, these equations simply fail in the prediction since the Pitzer equations cannot be applied to accurately determine the activity coefficients for all the aqueous species.

These drawbacks are overcome using a more powerful thermodynamic tool i.e. the concepts of statistical thermodynamics in the modeling of the sorption processes. In this work a model for the sorption of aqueous species into the solid phase is presented. The model was originally formulated to describe the sorption of ions and complexes onto activated carbon and ion exchange resins. Its complete derivation was presented by De Kock (1995) and recently reformulated by Lukey et al. (2000). This model is applied to the sorption of copper and nickel, and copper and iron, onto two ion exchange resins. These systems have been investigated for cyanide recycling from solutions containing high copper content and minor amounts of iron and nickel, typical of a Brazilian gold-copper mine (Leão and Ciminelli, 2000; Leão et al., 2000a).

MODEL DESCRIPTION

The model considers that the aqueous phase is ideal and all non-ideal behavior is accounted for in the resin phase. The approach, based on the minimization of free energy associated with the sorption step in the resin
phase, is derived from the application of Statistical Thermodynamics to the absorption of gases in liquids and solids.

The model is based on the following assumptions:

- The probability (P) that a molecule (I) sorbs on an active site is equivalent to the total fractional coverage of all the active sites. Mathematically:

\[ P(I_{\text{act}}) = x_i \]  

- The probability of a change in the total energy of the system is determined through the Boltzmann criterion:

\[ P(\text{change}) = \min \{ \exp(-\Delta E^*) I \} \]  

If \( \Delta E^* \) is negative, a value larger than unity is obtained for the exponential term. This implies a reduction in the total energy of the system and so a change in the system configuration is accepted. If \( \Delta E^* \) is positive, the exponential term will vary between 0 and 1, indicating a varying probability that the change will occur.

- The energy of the system is represented in a dimensionless form:

\[ E^* = \frac{E}{kT} \]  

- The solvent is considered as an additional species, designated as species "0".

- The probability of the species "I" being replaced by species "J" on the resin is calculated using the following equation:

\[ P(I \rightarrow J) = P(I_{\text{sol}}) \cdot P(I_{\text{act}}) \cdot P(J \rightarrow I) \]  

where \( P(I_{\text{sol}}) \) is the probability that species "I" in the bulk phase collides with an active site on the resin; \( P(I_{\text{act}}) \) is the probability that species "I" sorbs onto an active site; and \( P(J \rightarrow I) \) is the probability that species "I" will be replaced by species "J" if it is known that a collision occurs.

- The probability that an increase or decrease in sorption of species "I" will occur is calculated as the probability that the species "I" will replace any other molecule on the resin, including a molecule of the same species.

- All sites are available for sorption. At equilibrium, the probability that an increase or a decrease in the loading will occur on the resin must be equal.

For a system containing \( n \) species, it can be written:

\[ \sum_{j=0}^{n} x_j = 1 \Leftrightarrow x_0 = 1 - \sum_{j=1}^{n} x_j \]  

At equilibrium:

\[ \sum_{j=0}^{n} P(I \rightarrow J) = \sum_{j=0}^{n} P(J \rightarrow I) \]  

\[ P(I_{\text{sol}}) \cdot P(I \rightarrow J) = P(J \rightarrow I) \cdot P(J \rightarrow I) \]  

\[ x_i \cdot \sum_{j=0}^{n} y_j \cdot P(I \rightarrow J) = x_i \cdot \sum_{j=0}^{n} x_j \cdot P(J \rightarrow I) \]  

From the mass balance:

\[ x_i \cdot \sum_{j=0}^{n} y_j \cdot P(I \rightarrow J) = x_i \cdot \sum_{j=0}^{n} x_j \cdot P(J \rightarrow I) \]  

A set of linear equations is generated which can be solved using linear algebra:

\[ M \cdot X = D \]  

where \( X \) is a column vector containing elements \( x_i \), \( i = 1 \ldots n \); \( D \) is a column vector containing the probability that the solvent will be replaced by the \( i \)th species in the event of collision for \( i = 1 \ldots n \); and \( M \) is a square matrix with the following values:

\[ \text{cell}[i,j] = P(0 \rightarrow I) - P(J \rightarrow I) \]  

\[ \text{cell}[i,i] = P(0 \rightarrow I) + \sum_{j=0}^{n} y_j \cdot P(I \rightarrow J) - 1 \]

By solving this set of equations, the surface composition for systems with homogeneous solids and where no selective sorption takes place, can be predicted. However, to describe real systems, far from ideality, non-ideal effects must be also considered. These are described in the following paragraphs:

1. **Lateral interactions**: The Coulombic interaction between sorbed species on the resin may be significant and therefore these possible interactions must be incorporated into the model. Intuitively, more positive interaction energies would be expected for systems where the sorbed molecules are in close proximity. This is because the sorbed
species strongly interact, leading to an increase in total system energy. Mathematically:

\[ E_{i,\text{corr,Obs}} = E_{i,\text{corr,0}} + z \sum_{j=0}^{n} x_j \cdot I_{i,j} \]  

(14)

The interaction energy between two dissimilar molecules is estimated from the following equation:

\[ I_{i,j} = \sqrt{I_{i,i} \cdot I_{j,j}} \]  

(15)

2. Heterogeneous surfaces: Heterogeneous surfaces are modeled by dividing the surface of the sorbent into a series of equally sized homogeneous patches. The energy of each homogeneous patch is determined from a statistical distribution. In the present work it has been found that the Cumulative Normal distribution function (Eqn. 16) adequately describes the heterogeneous surface of each resin studied.

\[ \frac{1}{\sigma \cdot (2\pi)^{1/2}} \int_{-\infty}^{x} \exp \left[ -\frac{(x - \mu)^2}{2 \cdot \sigma^2} \right] dx \]  

(16)

3. Selective sorption: Selective sorption is associated with particular features of the sorption sites on the resin, for example steric effects or the nature of the matrix. To incorporate selective sorption into the model, each patch is divided into separate areas according to the number of species being modeled. The equilibrium loading of each species in each area can then be determined. This allows an estimate of the loading for each patch to be made using the relative size of each area to perform a weighted summation.

A detailed description of the algorithm used to solve the model is given by Lukey et al. (2000). In order to model the surface heterogeneity, the surface of the resin is divided into a set of homogeneous patches. Each patch is then divided into areas in order to model the selective sorption. The loading of each area is then calculated. The loading of the whole patch can then be determined using a weighted average for the areas considered. When the loading of all patches is determined an average is calculated for the whole surface. The model sets a value for the sorption energy and the composition of the resin phase is determined following the above-mentioned procedure. If the composition of the resin phase agrees with the experimental values, a final value for the parameters is produced. If the values of the experimental and the predicted values do not match, a new set of values is chosen and the procedure is repeated until there is a convergence with the experimental values. The estimation of the parameters is carried out through the minimization of the following objective function (OF):

\[ OF = \sum_{j=1}^{m} \sum_{i=1}^{n} (x_{i,\text{exp},j} - x_{i,\text{pred},j})^2 \]  

(17)

MODELING THE SORPTION ONTO ION EXCHANGE RESINS

The following examples discuss the application of the model to the sorption of metal cyanocomplexes onto ion exchange resins. The resins used are Imac HP555s (macroporous, polystyrene, triethylammonium) and Amberlite IRA958 (macroporous, polyacrylic, trimethyl ammonium). The experimental set-up is described by Lukey et al. (2000).

Copper-Nickel System

Previous work has shown that despite the presence of two copper complexes, Cu(CN)\(_{3}^{2-}\) and Cu(CN)\(_{4}^{3-}\), in the aqueous phase, the sorption of copper on the Imac HP555s resin is characterized by the presence of only the Cu(CN)\(_{3}^{2-}\) copper complex (Leão et al., 2000b). The preferential loading of the tricyano complex is due to the presence of the ethyl groups on the resin that hinders the uptake of the other copper complex. Nickel sorbs on Imac HP555s as the divalent Ni(CN)\(_{4}^{2-}\) species (Leão et al., 2000b).

Table I presents the model parameters obtained for the equilibrium sorption of copper and nickel onto the Imac HP555s resin. A Normal distribution was used to describe the heterogeneity of the surface for both metals. Since only Cu(CN)\(_{3}^{2-}\) and Ni(CN)\(_{4}^{2-}\) complexes sorbed onto the resin, a unimodal distribution was used to characterize the surface heterogeneity. A standard deviation of 0.03 was used for nickel, while for copper this value was set at 0.1. The higher value chosen for copper reflects the greater heterogeneity of the surface experienced by copper due to the presence of Cu(CN)\(_{3}^{2-}\) and Cu(CN)\(_{4}^{3-}\) in solution, while for nickel, only one species is observed in both the resin and the solution phases.
Table I: Parameters used for the modeling of copper and nickel sorption on Imac HP555s resin.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Solvent</th>
<th>Nickel</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy distribution</td>
<td>Normal</td>
<td>Normal</td>
<td>Normal</td>
</tr>
<tr>
<td>Mean</td>
<td>-</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>-</td>
<td>0.03</td>
<td>0.1</td>
</tr>
<tr>
<td>Selective sorption (%)</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

Species

<table>
<thead>
<tr>
<th>Surface</th>
<th>Solvent</th>
<th>Nickel</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean sorption energy</td>
<td>0</td>
<td>-18.24</td>
<td>-15.99</td>
</tr>
<tr>
<td>Interaction energies</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Similar to the sorption onto the Imac HP555s resin, nickel sorbs onto Amberlite IRA958 only as Ni(CN)$_4^{2-}$. Therefore a unimodal Normal distribution was used to describe the surface heterogeneity of the resin experienced by the nickel cyanide complex (Table II). In contrast, Raman studies have shown that the two copper complexes sorb onto the Amberlite IRA958 resin (Leão et al., 2000b). The presence of these two cyanocomplexes of copper is represented in the model by a bimodal Normal distribution. The bimodal Normal distribution is the weight sum of two single distributions. The first one (μ=0.8, σ=0.05) is associated with Cu(CN)$_3^{2-}$. Its weight in the bimodal Normal distribution is 0.35. The second distribution (μ=1.0, σ=0.2) represents the heterogeneity experienced by Cu(CN)$_4^{3-}$.

Although the nickel cyanocomplex is square planar and the Cu(CN)$_3^{2-}$ complex is trigonal planar, the model indicates that the selective sorption of either complex does not take place on the Imac HP555s or Amberlite IRA 958 resins (Tables I and II). This behavior can be explained by the nature of the resins studied. For the Imac HP555s resin, the most important factor is the electrical charge of the complex. Due to the double charges of Cu(CN)$_3^{2-}$ and Ni(CN)$_4^{2-}$, at least two functional groups must be in close enough proximity for sorption to take place, while for Cu(CN)$_4^{3-}$, sorption would require at least three triethyl groups to be in close proximity for sorption to occur. This is hindered by the steric effects associated with the triethyl functional group. In addition, the Cu(CN)$_4^{3-}$ complex is labile and so readily converts to the more stable tricyanocuprite complex in order to sorb onto the resin.

The selective sorption of either copper or nickel is not expected to take place in the Amberlite IRA958 system because this resin is hydrophilic and contains the trimethylammonium group. As a consequence, the affinity of the resin for copper or nickel cyanide complexes is not affected by their geometry or extent of co-ordination. In fact the hydration of both the resin and the complexes are credited to be the main parameters responsible for the sorption.

Comparing the mean sorption energies of copper and nickel for the two resins studied (Table I and Table II), it can be seen that these values are more negative for the Amberlite IRA958 resin than for the Imac HP555s resin. This is due to the difference in resin matrix and also to the functional group on each of the two resins. Amberlite IRA958 has a greater hydrophilicity due to its polyacrylic matrix compared with the polystyrene-based Imac HP555s, and that favors the sorption of copper. The fit of the model to the experimental data is presented in Figures 1 and 2.

Figure 1: A comparison between predicted and experimental copper and nickel loading on the resin Imac HP555s.
Copper-Iron System

The parameters used to model the equilibrium sorption of copper and iron on the Imac HP555s resin are presented in Table III and the fit to the experimental data is shown in Figure 3. In the copper-iron system, copper shows the same behavior as observed in the copper-nickel system, i.e. the presence of only the Cu(CN)₃⁻² complex on the Imac HP555s resin. For this reason a unimodal Normal distribution was used to model the sorption of copper. Using Raman spectroscopy, it has been observed that iron sorbs onto the resin as both Fe(CN)₆⁴⁻ and Fe(CN)₆⁻³ (Leão et al., 2000c). Similar to the modeling of the sorption of copper onto the Amberlite IRA 958 resin, a bimodal Normal distribution was applied to describe the heterogeneity experienced by iron cyanide. It is not possible to determine the ratio of these sorbed species on the resin and so an approximated fraction of 0.5 of each distribution was used in the model.

Table III. Parameters used to model the equilibrium sorption of copper and iron on Imac HP555s resin.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Solvent</th>
<th>Iron</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy distribution</td>
<td>- Normal Normal Normal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Distribution fraction</td>
<td>- 0.5 0.5 -</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>- 1 1.5 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard deviation</td>
<td>- 0.2 0.2 0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Selective sorption(%)</td>
<td>- 85 100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specie</td>
<td>Mean sorption energy</td>
<td>-13.58 -20.91</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Interaction energy</td>
<td>-0.31 1.26 1.21</td>
<td></td>
</tr>
</tbody>
</table>

Limiting the surface area available for the sorption of iron to 85% is now feasible, contrary to the copper-nickel system. This is because the iron cyanide complex is larger in geometry than the copper cyanide complex - Cu(CN)₃⁻² is a trigonal planar complex, while the ferricyanide and ferrocyanide complexes are octahedral in structure. The selective sorption parameter for iron (Table III) indicates that only 85% of the total surface area of the resin, which is available for the sorption of copper and iron, is actually available for the sorption of iron. The steric effects associated with the triethyl functional groups on this resin are responsible for the selectivity observed in this system, and as a consequence, the low iron uptake. It can be seen from Table III that the mean sorption energy of copper is more negative than that for iron. These values confirm that the Imac HP555s resin has a higher affinity for copper than iron. The interaction terms indicate that the sorbed complexes strongly repel each other, which leads to an increase in total system energy. This is expected due to the high charge of these complexes.

The parameters used to model the equilibrium sorption of copper and iron onto the Amberlite IRA958 resin are shown in Table IV. The model fit is shown in Figure 4. Due to the presence of Cu(CN)₅⁻² and Cu(CN)₆⁻³ on the resin, a bimodal Normal distribution was used to describe the energy distribution for copper. A unimodal Normal distribution was used for iron because it has been shown previously that it sorbs onto the resin only as Fe(CN)₆⁻⁴. In this system, the steric effects observed for the sorption of iron onto the Imac HP555s resin are not important.
Table IV. Parameters used to model the equilibrium sorption of copper and iron on Amberlite IRA 958.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Iron</th>
<th>Copper</th>
<th>Cu(CN)$_3$$^2$</th>
<th>Cu(CN)$_6$$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy distribution</td>
<td>-</td>
<td>Normal</td>
<td>Normal</td>
<td>Normal</td>
</tr>
<tr>
<td>Distribution fraction</td>
<td>-</td>
<td>-</td>
<td>0.35</td>
<td>0.65</td>
</tr>
<tr>
<td>Mean</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>-</td>
<td>0.2</td>
<td>0.05</td>
<td>0.2</td>
</tr>
<tr>
<td>Selective sorption (%)</td>
<td>95</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Species</td>
<td>Mean sorption energy</td>
<td>-0.25</td>
<td>-19.60</td>
<td>-13.20</td>
</tr>
<tr>
<td>Interaction energy</td>
<td>1.00</td>
<td>1.02</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A better fit of the model is obtained when the surface area available for the sorption of iron is restricted to 95% of the total surface area available for sorption. This is reasonable because it has been shown previously by Leão and Ciminelli (2000) that the Amberlite IRA 958 resin is less selective than the Imac HP555s resin. The greater affinity of the Amberlite IRA 958 resin for iron was reflected in the model by the more negative mean sorption energy of iron.

The interaction energy terms presented in Tables III and IV are related to the Coulombic forces present between sorbed complexes on each resin. More positive values for the interaction parameters are expected when the metal concentration on the resin is high, and also when more negatively charged complexes are sorbed onto the resin. For example, the interaction energies of the copper-iron system are greater than zero because both resins studied sorb the highly charged iron cyanide complex. As mentioned previously, a value greater than zero for the interaction parameters indicates that the sorbed species on the resin strongly repel each other, thereby destabilizing the system. In contrast, if the interaction parameter is less than zero, then the sorbed complexes interact in a way which leads to a lower total system energy.

CONCLUSIONS

A probabilistic model developed to predict multicomponent equilibria has been applied to the sorption of cyanocomplexes onto ion exchange resins. The sorption of complexes in highly non-ideal systems can be accurately described by model parameters that have a fundamental meaning. The results of the present work show a more negative sorption energy for nickel compared to copper, and copper compared to iron, in triethylammonium resins (Imac HP555s). Moreover, a more negative sorption energy for copper compared to nickel, and iron compared to copper, in polyacrylic resins (Amberlite IRA 958) is observed. The Normal distribution is used to characterize the surface heterogeneity experienced by the cyanocomplexes during sorption. The mathematical model can be used to successfully describe the equilibrium sorption of cyanocomplexes onto ion exchange resins and also other sorbents.

ACKNOWLEDGEMENTS

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NOMENCLATURE

P  Probability
\( x_i \)  Equivalent mole fraction of species \( i \) in the solid phase.
\( y_i \)  Equivalent mole fraction of the species \( i \) in the aqueous phase.
\( E^* \)  Dimensionless sorption energy.
\( E \)  Sorption energy, J/K.
\( k \)  Boltzmann constant.
n  Total number of species in the system.
m  Total number of experimental data points.
z  The number of nearest neighboring sites on the surface.
\( I_{ij} \)  Interaction energy between species \( i \) and \( J \).
\( T \)  Absolute temperature, K.
\( \sigma \)  Standard deviation.
\( \mu \)  Mean.

REFERENCES


