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Modeling of ionic equilibria of trace metals (Cu^{2+}, Zn^{2+}, Cd^{2+}) in concentrated aqueous electrolyte solutions at 25 °C

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Abstract

This work presents a model of activity coefficients and a database for ionic equilibria of Cu^{2+}, Zn^{2+}, and Cd^{2+} in (H^+, Na^+, K^+, Mg^{2+}, Ca^{2+})(OH^-, Cl^-, NO_3^-, ClO_4^-, HSO_4^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}) aqueous media valid up to 6–12 m ionic strength. The activity coefficient of a dissolved species is represented by empirical equation $\ln\gamma_i = -(A_\gamma/2)z_i^2(I - I\exp(-8I^{0.5}))^{1/3} + \sum b_{ij}m_j$, where A_γ is Debye–Hückel constant (1.17 at 25 °C), γ_i and z_i are activity coefficient and charge of a dissolved species i, I is molal ionic strength, b_{ij} is model parameter, and m_j is molal concentration of dissolved species. The model is applicable to the modeling of ionic equilibria, as well as to simulation of solubility of salts in mixed electrolyte solutions.

Keywords: Activity coefficient; Ionic strength; Copper; Zinc; Cadmium; Hydrolysis; Chloride; Sulfate; Carbonate; Complex; Constant

1. Introduction

Different heavy metals, such as copper, zinc, and cadmium, are often used as probes for studies of adsorption properties of various solid–water interfaces. These metals are adsorbed at different pH values. This is very useful for understanding adsorption mechanisms. Adsorption studies demand the careful calibration of these “instruments,” i.e., accurate estimation of the metal ion activity in solution. Also, the adsorption effects should be distinguished from the precipitation of solids. For these purposes, I have constructed a model of activity coefficients and a database for ionic equilibria of Cu^{2+}, Zn^{2+}, and Cd^{2+} in (H^+, Na^+, K^+, Mg^{2+}, Ca^{2+})(OH^-, Cl^-, NO_3^-, ClO_4^-, HSO_4^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}) media valid up to 6–12 m ionic strength. Besides the most important natural salts such as chlorides, sulfates, and carbonates, this system includes the “noncomplexing” salts widely used for potentiometric studies (perchlorates and nitrates). For instance, the majority of apparent formation constant of different species was measured in sodium perchlorate solutions. For example, there is no problem in estimation of cadmium ion activity in sodium perchlorate solution in the presence of chloride ions. However, the constants of the cadmium chloride complexes measured in sodium perchlorate medium are not valid for sodium chloride solution, and the estimation of cadmium activity in sodium chloride solution is a puzzle. Thus, this puzzle should be solved with use of model applicable for mixed electrolyte solutions.

The estimation of activity coefficients is a complex problem. At low ionic strengths (0–0.1), it may be solved with the use of an “average” activity coefficient (e.g., [1]). At 1 m ionic strength, this approach is still efficient (accuracy of estimation of formation quotients is generally better than ±0.2 log units), but at 6 m ionic strength the uncertainty rises to ±1 log unit. Therefore, at elevated ionic strengths, an extended model of activity coefficients is necessary.

The Pitzer model [2] is convenient for calculating mean activity coefficients of electrolytes from water activity in solution. This model accurately describes the experimental data, and the set of the Pitzer parameters may be used as an

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alternative to the database of experimental data on activity coefficients of single and mixed electrolytes. Calculations with the Pitzer model require at least two model parameters for each cation–anion combination. However, the majority of such combinations are represented by combinations of trace species (e.g., $ZnOH^+$—anion, $Cu(CO_3)_2^{2-}$—cation, etc.). For example, at the Cd adsorption from (Na, H)(Cl, OH) solution onto some solid, the major ions are H^+, Na^+, Cl^-, and OH^-, whereas the trace species are Cd^{2+}, $CdOH^+$, Cd_2OH^{3+}, $Cd(OH)_2^0$, $Cd(OH)_3^-$, $Cd(OH)_4^{2-}$, $CdCl^+$, $CdCl_2^0$, $CdCl_3^-$, and $CdCl_4^{2-}$. The thermodynamic constants in this system are known with low accuracy, and the dependence of the formation quotients on NaCl concentration is not known. Thus it is impossible to establish the Pitzer parameters for all of these species. This makes the Pitzer model almost useless for studies of trace elements in solution. Because of this, less accurate but simpler approaches are more efficient for such studies.

The specific interaction theory (SIT) approach (see Ref. [3]), which was developed by Brønsted, Guggenheim, and Scatchard, is very attractive because of its simplicity and general applicability in description of ionic equilibria. Within the SIT approach, the activity coefficient of some ion, γ_i, may be calculated from the equation

$$\log\gamma_i = z_i^2 D + \sum \varepsilon_{ij} m_j. \tag{1}$$

Here z_i is the charge of the ion, $D = -0.51I^{0.5}/(1 + 1.5I^{0.5})$ is the electrostatic term common to all ions (I is molal ionic strength), m_j is the molality of a counterion, and $\varepsilon_{ij} = \varepsilon_{ji}$ is a model parameter. The values of parameters ε_{ij} for cation–anion combinations may be found in Ref. [3]. Within the SIT approach, the parameters for cation–cation and anion–anion combinations are neglected. In fact, the mixing parameters of the electrolytes are generally small. However, some of them are significant, and this makes the SIT approach inapplicable to the modeling of some ionic equilibria (e.g., dissociation of water). Also, the electrostatic term of SIT approach does not allow accurate description of the single electrolyte activity data. In the present study, I have improved this approach in order to obtain a more careful description of experimental data and retain the simplicity of Eq. (1). All values (constants, solubility, activity coefficients, parameters, etc.) refer to temperature 25 °C, if not otherwise indicated.

2. Model description

It is known that the activity coefficient of neutral species in salt solution may be simulated with the use of "salting coefficients." For example, the following equation is efficient for simulation of CO_2 solubility in salt solutions (Fig. 1):

$$\ln\gamma_i = \sum b_{ij} m_j. \tag{2}$$

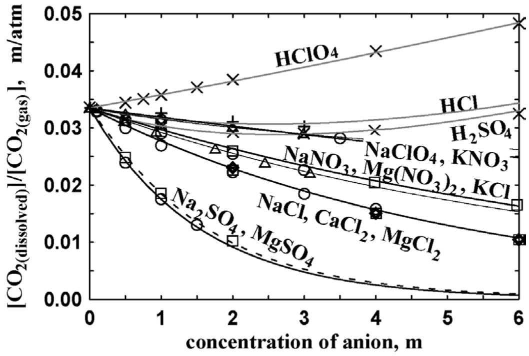

Fig. 1. Solubility of carbon dioxide in $NaClO_4$ [4], HCl, $CaCl_2$, $MgCl_2$ [5], NaCl, $NaNO_3$, Na_2SO_4, KCl, KNO_3, $Mg(NO_3)_2$, $MgSO_4$ [6], $HClO_4$ and H_2SO_4 [7] solutions.

Here γ_i is the activity coefficient of dissolved carbon dioxide, b_{ij} is a salting coefficient, j is an ion, and m_j is the molality of an ion. It is interesting that the solubility of carbon dioxide is almost insensitive to the nature of the cation except for potassium and proton.

In H_2SO_4 solution, Eq. (2) gives no satisfactory description of experimental data, because the cumulative activity coefficient of $CO_{2(aq)}$ increases up to 3 m H_2SO_4 and then decreases. However, one may suggest that Eq. (2) is valid in all cases, if account is taken of the HCO_2^+ complex. Similarly, one may suggest that Eq. (2) is true for ionic species, if account is taken of association and electrostatic interactions. Thus, Eq. (2) may be used to obtain the optimal equation for the electrostatic term.

Before the Debye–Hückel theory was developed, the most serious attempt to describe the electrostatic interactions of ions in solution was undertaken by Ghosh [8]. He suggested that ions in solution are located on a kind of solid crystal, and the electrostatic energy may be calculated by the use of this analogy. Using a similar approach, Bjerrum [9,10] suggested an equation for the activity coefficients of diluted 1–1 electrolytes at 25 °C:

$$\log\gamma_i = -BC^{1/3}. \tag{3}$$

Here C is the molar concentration of the 1–1 electrolyte, and B is a constant. As estimated by Bjerrum from experimental data, $B = 0.25$ at 25 °C. The constant B is dependent on the assumed structure of the solution. If each ion is surrounded by four counterions (analogous to the CuCl lattice, the Madelung constant 1.638 [11]), the theoretical value of the constant B is 0.313. At coordination number 6 (analogous to the NaCl lattice, the Madelung constant 1.748 [11]), the theoretical value of constant B is 0.289. At coordination number 8 (analogous to the CsCl lattice, the Madelung constant 1.763 [11]), the constant B should be calculated at 0.267. It can be seen that theoretical estimates of constant B are close to the experimental value. However, there is no possibility of calculating a unique value of parameter B for each electrolyte. Thus, parameter B is an empirical one.

Bjerrum's equation carefully describes the electrostatic interactions up to very high ionic strengths [10], but is not