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Computer Modeling and Speciation

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Abstract: The models use the law of mass action and mass balance and thermodynamic formation constants for all of the possible metal-ligand species, in conjunction with defined parameters such as pH, redox potentials and total metal and total ligand concentrations. In any assessment of real-life processes made using simulation techniques, there are three major sources of uncertainty. These have been referred to [19] as modeling, data and completeness uncertainties. Modeling uncertainties stem from an imperfect understanding of the processes being modeled and/or from numerical approximations used in the mathematical representations of processes.

Introduction:

Chemical speciation is often studied by using experimental methodology; however, an alternative approach involves the application of theoretical chemical concepts to predict the distribution and transformations of chemical species, usually by calculating the concentrations of species in equilibrium. For gas-phase equilibria, it is convenient to minimize the free energy of the system by adjusting the partial pressures of the reagents, using either stoichiometries based on explicit chemical reactions or a non-stoichiometric approach in which chemical reactions are not used explicitly [1].

Such an approach is convenient because there are extensive databases of standard free energies of formation for compounds in the gas phase and (for ideal-gas mixtures) there is a simple relationship between the chemical potential of a species, its standard free energy of formation and its partial pressure. For equilibria in solution, usually the equilibrium constants are measured for the individual reactions and the species concentrations are calculated by solving the mass-balance equations. This approach was pioneered in the programs HALTAFALL [2] and COMICS [3], which were written to solve sets of equations that typically might arise with systems of one or two metal ions and one or two ligands. Although they could be adapted to deal with slightly larger numbers of components, they could not be greatly expanded. In particular, they were both rather limited in respect of the way they stored data and in respect of their equation-solving algorithms [4]. Since the development of these programs and with advances in computer speed and availability, a number of computer programs for the simulation of metal-ligand equilibria in aqueous systems have been developed. These include ECCLES [5], MINEQL [6], SCOGS [7], SOLMNQ [8], COMPLOT [9], SPE [10], ESTA [11], GEOCHEM [12], JESS [13], visual MINTEQ [14], CHEAQS [15] and HYSS [16]. They are static models which calculate the chemical equilibrium distribution of aqueous species in a solution and in some cases, the saturation indices for solid phases.

Other programs such as PHREEQC [17] and EQ3/6 [18] perform the same function as the chemical speciation models but, in addition, they may be used as dynamic models capable of predicting the path of a reacting system. For example, mass transfer in and out of a system, or changes in the distribution of an aqueous species, either as a reaction progresses or with time. Although the speciation models mentioned above vary in sophistication, the basic components of each of the models are the same (Fig. 1). The models use the law of mass action and mass balance and thermodynamic formation constants for all of the possible metal-ligand species, in conjunction with defined parameters such as pH, redox potentials and total metal and total ligand concentrations. In any assessment of real-life processes made using simulation techniques, there are three major sources of uncertainty. These have been referred to [19] as modeling, data and completeness uncertainties. Modeling uncertainties stem from an imperfect understanding of the processes being modeled and/or from numerical approximations used in the mathematical representations of processes. Data uncertainties arise as a result of poor quality and/or applicability of data/parameters used as input to a mathematical model. Completeness uncertainties refer to possible omission from the model because of lack of knowledge.

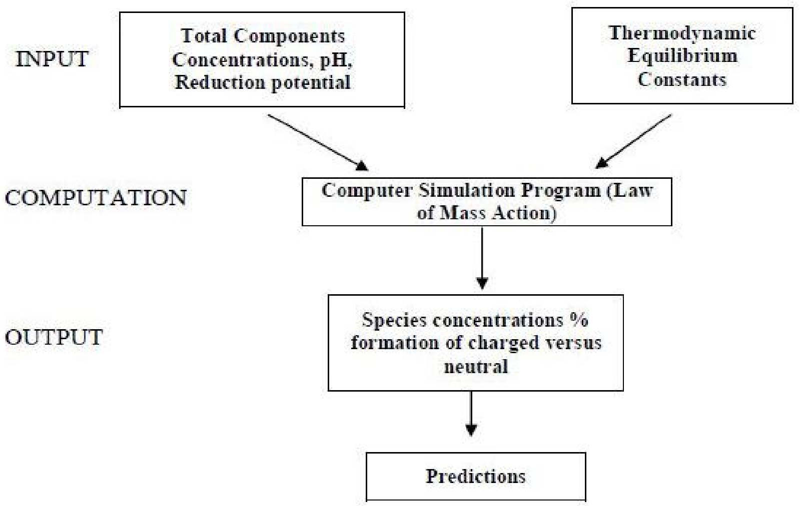

Fig. 1: Basic components of a chemical speciation model

The contribution of each type of uncertainty to the overall uncertainty which is intrinsic to a given simulation exercise will vary depending upon the process being modeled. The total of these uncertainties associated with a model can be quantified by a combination of uncertainty analysis and exercises in verification and validation [19]. Verification and validation exercises compare the models and their predictions with experimental results.

These procedures are also used in comparisons to further assess the success, or otherwise, of calculation procedures [20]. In simulations of chemical speciation in aqueous media, the main source of uncertainty is normally the quality of the input data, specifically that of the formation constants and the composition of their associated complexes. Thus, it is essential that the formation constants used in any chemical speciation modeling are critically evaluated. In evaluating formation constants from any source, factors that are considered include: experimental method, purity of reagents, background electrolyte, reagent concentrations, ionic strength and computational procedures.

Software for Modeling Complex Equilibria: Glass electrode measures protons associated with the solvent (including those in looser combinations); NMR, on the other hand, measures only strongly bound protons, while photometric method monitors in an intermediate way. A perusal of the literature [21-24] revealed that potentiometry using glass electrode gained wide popularity in the determination of equilibrium constants in preference to spectrophotometry, because the number of unknown quantities (extinction coefficient and stability constant) is double in the latter. However, with the advances in optimization methods for a large number of variables, model-free data treatment [25] and automation in data acquisition systems [26-30], Kaden and Zuberbuhler advocated [31] hyphenated spectro-pH meter. Although proton NMR was employed to calculate microionization constants in yester years, ^{17}O and ^{15}N paramagnetic transverse relaxation time [32] or ESR titrations [33] at ambient temperature were introduced as new techniques to calculate stability constants of protonated and/or hydroxylated complexes.

Formulation of Mathematical Model

For simplicity of mathematical treatment, the interaction of a metal ion with a ligand (LH_h) is considered and the same treatment can be extended to other species encountered in complex equilibria of mononuclear complexes summarized in Table 1.

The interaction of metal ion, with most anionic form of the ligand and proton(s) in solution phase results in NB complexes and the equilibrium for the formation of the jth species is represented by Eq. 2.1.

Table 1: Types of species likely to be encountered in complex equilibrium of mononuclear complexes.

Species	Stoichiometric coefficients			
	m	l	h	x
Metal hydrolysis	1	0	<0	0
Binary complexes (a) Unprotonated, unhydroxylated (ML_n)	1	>0	0	0
(b) Protonated	1	>0	>0	0
(c) Hydroxylated	1	>0	<0	0
Ternary complexes (a) Unprotonated, unhydroxylated (ML_n)	1	>0	>0	>0
(b) Protonated	1	>0	>0	>0
(c) Hydroxylated	1	>0	<0	>0
m, l, x, h: Stoichiometric coefficients of metal, primary ligand, secondary ligand and hydrogen, respectively				

$$m(j)M + l(j)L + h(j)H \Leftrightarrow M_{m(j)}L_{1(j)}H_{h(j)} \qquad (2.1)$$

Then the formation constant for the j^{th} species can be written as

$$\beta_{m(j)l(j)h(j)} = \frac{M_{m(j)}L_{l(j)}H_{h(j)}}{FM_i^{\,m(j)} * FL_i^{\,l(j)} * FH_i^{\,h(j)}}$$

$$= \frac{CS_{j,i}}{FM_i^{\,m(j)} * FL_i^{\,l(j)} * FH_i^{\,h(j)}} \qquad (2.2)$$

where, FM_i and FL_i are the free concentrations of metal ion and ligand and $CS_{j,i}$ is the concentration of j^{th} complex at i^{th} experimental point: h(j) is negative for hydroxylated species. A titrand of total volume, V_0 containing an indifferent electrolyte, V_m cm^3 of metal ion (C_M mol dm^{-3}) and V_l cm^3 of ligand (C_L mol dm^{-3}) is titrated with alkali of concentration, ALK. If β_i is the pH meter dial reading after equilibration (detected by successive reading not differing by 2 or 3 times the readability of pH meter) for V_i cm^3 of alkali added, the total concentrations at i^{th} experimental point are given by

$$\left.\begin{aligned} TME_i &= V_m * C_M / (V_0 + V_i) = TM0 * V_0 / (V_0 + V_i) \\ TLE_i &= V_l * C_L / (V_0 + V_i) = TL0 * V_0 / (V_0 + V_i) \\ THE_i &= \frac{V_A * C_A}{V_0 + V_i} - \frac{ALK * V_i}{V_0 + V_i} + NDP * TLE_i + OH_i \end{aligned}\right\} \qquad (2.3)$$

where TM0 and TL0 are the analytical concentrations of metal and ligand in V_0 cm^3 of solution. The calculated total metal ion concentration is

$$\begin{aligned} TMC_i &= FM_i + \sum_{j=1}^{NB} m(j) * \beta_{m(j)l(j)h(j)} * FM_i^{m(j)} * FL_i^{l(j)} * FH_i^{h(j)} \\ &= FM_i + \sum_{j=1}^{NB} m(j) * CS_{j,i} \qquad (2.4) \end{aligned}$$

Similarly for ligand and hydrogen ion, the corresponding equations are

$$\left.\begin{aligned} TLC_i &= FL_i + \sum_{j=1}^{NB} l(j) * CS_{j,i} \\ THC_i &= FH_i + \sum_{j=1}^{NB} h(j) * CS_{j,i} + OH_i \end{aligned}\right\} \qquad (2.5)$$

If the free concentrations of all the three ingredients (ligand, metal and hydrogen ion) are monitored, it is sufficient to consider NB points. Solving of simultaneous linear equations [34] gives the formation constants. If several data points, NP, are available then $^{NP}C_{NB}$ sets of stability constants result and, therefore, some statistical criteria are to be applied to arrive at the best parameters [35]. In many cases the determination of metal ion and free ligand concentration becomes difficult. Then hydrogen ion concentration is the only parameter that can be monitored and, hence, non-linear mass-balance equations have to be solved.

A large number of computer programs are available ranging in application from calibration of glass electrode [36] to modeling strategies [37-40] applicable to quaternary complexes containing protonated, hydroxylated and polynuclear species. All the programs adopt this mathematical model for the above tasks.

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