Unified Linear Predicting Models for the Essential Reactions of Metal Ions in Aquatic and Surface Systems

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This study shows that three molecular descriptors can be used to establish satisfactory linear free-energy relationships (LFER) allowing the quantitative modeling of essential reactions of metal ions in aquatic and surface systems. Namely, the Me−O bond length (R_{Me-O}), the water-binding energy (ΔE_{WB}) of monohydrated metal ions ($Me(H_2O)^{z+}$), and the lowest unoccupied molecular orbital energy of metal ions ($LUMO_{Me^{z+}}$), calculated with the nonlocal density functional method can serve as the three governing parameters in the present LFER. The feasibility of the LFER in evaluating the thermodynamic constants of the deprotonation, precipitation, complexation, solvation, diffusion, adsorption, and cation-exchange reactions of aqueous metal ions is also documented. This approach can be quite useful in universally elucidating the interrelationship among various chemical reactions of metal ions in aquatic and surface systems.

I. Introduction

The use of linear free-energy relationship (LFER) for predicting the formation free energy of inorganic solids has been developed by Sverjensky and Molling:[1]

$$\Delta G^{\circ}_{f,M_{\nu}X} = a_{M_{\nu}X}\Delta G^{\circ}_{n,M^{2+}} + b_{M_{\nu}X} + B_{M_{\nu}X}r_{M^{2+}} \qquad (1)$$

By dividing the free energy of formation of aqueous metal ions ($\Delta G^{\circ}_{f,M^{2+}}$) into the solvation part ($\Delta G^{\circ}_{s,M^{2+}}$) and the nonsolvation part ($\Delta G^{\circ}_{n,M^{2+}}$), $\Delta G^{\circ}_{n,M^{2+}}$ in eq 1 can be represented as $\Delta G^{\circ}_{n,M^{2+}} = \Delta G^{\circ}_{f,M^{2+}} - \Delta G^{\circ}_{s,M^{2+}}$. Here, $\Delta G^{\circ}_{f,M^{2+}}$ is derived from experiment whereas $\Delta G^{\circ}_{s,M^{2+}}$ can be calculated from the Born solvation free energy. $r_{M^{2+}}$ is the Shannon−Prewitt radius of the metal ion. The coefficients $a_{M_{\nu}X}$, $b_{M_{\nu}X}$, and $B_{M_{\nu}X}$ reflect the crystal structure of crystalline solids $M_{\nu}X$.

In addition, Sverjensky also separated the standard Gibbs free energy of sorption of divalent metal ions on several minerals into the classical Born solvation part and the nonsolvation part that is characteristic for a given divalent metal ion.[2] The thermodynamic equilibrium constant for sorption ($\log K_{int,j,k}$) can be expressed as

$$\log K_{int,j,k} = -\left(\frac{\Omega_j}{2.303RT}\right)\left(\frac{1}{\epsilon_k}\right) + \log K'_{ii,j} \qquad (2)$$

where Ω_j represents a conventional Born coefficient for the metal ion j. ϵ_k is the dielectric constant of the mineral solid k. The term $\log K'_{ii,j} = \log K_{ii,j} + \log K_{ifc,j,k}$. $\log K_{ii,j}$ is assumed to be a property of the metal ion alone. The term $\log K_{ifc,j,k}$ contains contributions from the dielectric constants of the bulk solvent and the interfacial water. It has been shown that $\log K'_{ii,j}$ values correlate linearly with $\Delta G^{\circ}_{n,j}$ values according to the following regression: $\log K'_{ii,j} = 0.016\Delta G^{\circ}_{n,j} + 5.901$. The nonsolvation free-energy contribution ($\Delta G^{\circ}_{n,j}$) is defined the same way as in eq 1.

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Their research clearly shows that it is possible to separate the solvation and nonsolvation energy terms in the standard Gibbs free energy of formation of aqueous metal ions or in the formation of metal ion/solid surface complexes in aquatic environments. However, in their approach, one needs to include explicitly the solvation and nonsolvation contributions to account for deviations from the observed free energy or the equilibrium constant. In the present study, we take a different approach to cover a broad range of chemical reactions of metal ions in aquatic and surface systems. In this paper, we introduce three descriptors of aqueous metal ions calculated easily by the density functional theory (DFT): (i) the lowest unoccupied molecular orbital energy of metal ions ($LUMO_{Me^{z+}}$), (ii) the Me−O bond length (R_{Me-O}) in monohydrated metal ions ($Me(H_2O)^{z+}$), and (iii) the water-binding energy (ΔE_{WB}) of monohydrated metal ions. (See Supporting Information, Figure 1S.) In this case, the water-binding energy of monohydrated metal ions can be obtained from the calculated energy change for the water-binding reaction: metal ion (Me^{z+}) + water molecule (H_2O) → monohydrated metal ion ($Me(H_2O)^{z+}$). The objective of this study is to examine the feasibility of the preset LFER to predict the thermodynamic constants of deprotonation, precipitation, complexation, solvation, diffusion, adsorption, and cation-exchange reactions of metal ions accurately.

II. Computational Methods

The nonlocal density functional of Becke is used for exchange, and the Perdew−Wang, for correlation. The calculations were performed using double-numerical basis sets augmented by polarization functions (DNP) but without the frozen-core approximation. The threshold of convergence of total energy in the self-consistent field (SCF) iterations was set at $10^{-6}E_H$. A BFGS Newton−Raphson minimizing scheme was used for the geometry optimization of monohydrated metal ions. The convergence criterion of the gradient with respect to internal coordinates was set at $10^{-3}E_H$ au^{-1}. To be able to compare the electronic structure between various monohydrated metal ions, the initial geometries were constrained to the same C_{2v} point-

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TABLE 1: Me$-$O Bond Length (R_{Me-O}), Water-Binding Energy (ΔE_{WB}) of Monohydrated Metal Ions, and the Lowest Unoccupied Molecular Orbital Energy of Metal Ions (LUMO$_{Me^{z+}}$) Calculated with the Becke$-$Perdew$-$Wang Nonlocal Density Functional Method

monovalent metal ion				divalent metal ion				trivalent metal ion			
metal ion	R_{Me-O} (Å)	ΔE_{WB} (kcal mol^{-1})	LUMO$_{Me^{z+}}$ (eV)	metal ion	R_{Me-O} (Å)	ΔE_{WB} (kcal mol^{-1})	LUMO$_{Me^{z+}}$ (eV)	metal ion	R_{Me-O} (Å)	ΔE_{WB} (kcal mol^{-1})	LUMO$_{Me^{z+}}$ (eV)
Li$^+$	1.865	-31.32	-6.469	Be^{2+}	1.506	-139.64	-20.199	Al^{3+}	1.789	-193.64	-31.998
Na$^+$	2.257	-20.71	-7.013	Mg^{2+}	1.934	-73.67	-18.078	Sc^{3+}	1.959	-171.05	-33.301
K$^+$	2.642	-14.65	-6.020	Ca^{2+}	2.204	-56.07	-16.643	Cr^{3+}	1.948	-283.37	-39.887
Cs$^+$	3.075	-10.74	-5.241	Sr^{2+}	2.411	-45.29	-13.950	Fe^{3+}	2.109	-243.71	-40.707
Ag$^+$	2.297	-24.49	-10.896	Ba^{2+}	2.618	-37.78	-13.718	Ga^{3+}	1.852	-221.43	-36.176
				Mn^{2+}	1.977	-81.77	-21.455	In^{3+}	2.083	-156.25	-31.999
				Co^{2+}	1.882	-108.86	-21.310	Y^{3+}	2.150	-116.63	-26.374
				Zn^{2+}	1.883	-101.40	-22.970	La^{3+}	2.360	-93.50	-24.258
				Cd^{2+}	2.154	-71.19	-20.648				
				Pb^{2+}	2.370	-54.11	-17.353				

group symmetry. All density functional calculations are carried out using the DMol version 960 program.[3,4] An example of input data (DMol.car and .input files) for the DFT runs is listed in Table 1S of Supporting Information.

III. Results and Discussion

Since the Becke$-$Perdew$-$Wang nonlocal density corrections take into account the nonuniform electron density in a molecular system, the total electronic molecular energies depend not only on the electron density itself but also upon its gradient.[3] This approach can thus lead to more stable equilibrium structures than the conventional local density functional (LDF) approximations.[5] The Me$-$O bond lengths (R_{Me-O}), the water-binding energies (ΔE_{WB}) of monohydrated metal ions, and the lowest unoccupied molecular orbital energies of metal ions (LUMO$_{Me^{z+}}$) calculated with the Becke$-$Perdew$-$Wang nonlocal density functional method using a high-level double-numerical plus p-polarization (DNP) basis set are listed in Table 1. Other calculated results are summarized in Table 2S of Supporting Information. The computed Me$-$O bond lengths agree well with the experimental values and the ab initio calculations.[6] They also reveal a good linear relationship with the Shannon$-$Prewitt radii of metal ions ($R_{Me^{z+}}$):

$$R_{Me-O} = 1.0872 R_{Me^{z+}} + 0.9984$$

$$\text{regression coefficient } (r) = 0.9644 \quad (3)$$

From a purely electrostatic viewpoint, it is the metal$-$oxygen interatomic distance or the corresponding radius of the metal ion that directly governs the strength of Columbic interactions between the central metal ion and adjacent negatively charged ionic groups such as the hydroxide ion, organic ligands, and surface hydroxyl groups. Furthermore, under quantum mechanical considerations, the metal$-$oxygen interatomic distance in aqueous solutions is influenced by the number of electrons, molecular orbital diffusibility, electron density distribution, and covalent bonding (i.e., electron sharing) effect. Hence, for a given coordination state, the Me$-$O bond length is closely related to the electronic structures of the metal aquo-ions with the corresponding cationic valence. It is therefore an important factor controlling the reactivity of the chemical reactions of the metal aquo-ions.

However, the energy change from the water-binding reaction of metal ions is also a useful indicator for quantifying the chemical reactivity of aqueous metal ions. In our previous studies,[7] the water-binding energy (ΔE_{WB}) of metal ions has been proven to correlate linearly with the observed deprotonation constants (pK_a) of aqueous metal ions. The global linear

relationship for the calculated water-binding energies and experimental deprotonation constants can be expressed as

$$pK_a = 0.0569 \Delta E_{WB} + 14.9930$$

$$\text{regression coefficient } (r) = 0.9721 \quad (4)$$

Within the framework of Fukui's frontier molecular orbital (FMO) theory,[8] the interaction energy (ΔE) of a chemical reaction can be obtained from the equation

$$\Delta E = \frac{2(\lambda_n \lambda_e \langle \psi_{HOMO} | \hat{H} | \psi_{LUMO} \rangle)^2}{(HOMO_n - LUMO_e) + \left(\dfrac{\rho_n \rho_e}{\epsilon R_{n-e}} \right)}$$

Here, λ represents the molecular orbital coefficient. The term $\langle \psi_{HOMO} | \hat{H} | \psi_{LUMO} \rangle$ is the resonance integral. The potentials coming from both the nucleophile and electrophile are contained in the potential Hamiltonian operator, $\hat{H}$. Here, ρ is the local charge density, ϵ is the dielectric constant, and R_{n-e} is the distance between the nucleophile (n) and electrophile (e). Several indices related to the HOMO$_n$ and LUMO$_e$ energies such as hardness, chemical potential, electronegativity, and softness have been proposed for assessing the chemical reactivity on the basis of density functional theory and Koopmans' theorem. A large body of literature uses the indices of hardness and chemical potential to indicate the reactivity of a chemical reaction and to describe the electronic characteristics of a molecular system. The concept of electronegtivity has been employed to represent the electron attractive capability of the constituent atoms in a molecule. Softness is one of the intrinsic properties of molecules that can imply the extent of chemical reactivity. For most of the aqueous reactions of metal ions, the water molecule usually acts as an important Lewis base (nucleophile), and the metal ion usually acts as a Lewis acid (electrophile). Since the HOMO energy of the water molecule is a constant (HOMO$_{H_2O} = -7.30$ eV), the LUMO energies of metal ions (LUMO$_{Me^{z+}}$) are therefore strongly correlated to the progress of aqueous reactions of metal ions.

The calculated results of the LUMO energies are correlated strongly with the cationic valence, ionic radius, and electron configuration of metal ions. (See Table 1.) Several trends can be summarized as follows: (i) the LUMO energies of higher-valence metal ions are lower than those of smaller-valence metal ions; (ii) the LUMO energies of metal ions with a smaller ionic radius are lower than those of metal ions with a larger ionic radius; (iii) the LUMO energies of metal ions with partially filled electronic shells are lower than those of metal ions with inert electronic configurations.

TABLE 2: Linear Predicting Models and Regression Coefficients (r) for the Thermodynamic Constants of Seven Chemical Reactions of Metal Ions

chemical reaction	linear model[a]	regression coefficient (r)	metal ion
deprotonation	$\log K_a = -0.36214 \text{LUMO}_{Me^{z+}} - 0.29336 R_{Me-O} + 2.22187 \times 10^{-4}\Delta E_{WB} - 16.38063$	0.9557	Li^+, Na^+, K^+, Ag^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}, Cr^{3+}, Fe^{3+}, Y^{3+}, La^{3+}
precipitation	$\log K_{sp} = 0.21754 \text{LUMO}_{Me^{z+}} - 2.65680 R_{Me-O} + 0.13338\Delta E_{WB} + 7.09591$	0.9711	Mg^{2+}, Ca^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Fe^{3+}
complexation	$\log K_{11} = -1.22078 \text{LUMO}_{Me^{z+}} - 0.87478 R_{Me-O} + 0.08180\Delta E_{WB} - 2.17735$	0.9601	Li^+, Na^+, K^+, Ag^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}, Cr^{3+}, Fe^{3+}, Y^{3+}, La^{3+}
solvation	$\Delta G°_{solv} = 42.53578 \text{LUMO}_{Me^{z+}} - 17.79250 R_{Me-O} - 0.43996\Delta E_{WB} + 138.76689$	0.9547	Li^+, Na^+, K^+, Cs^+, Ag^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}, Cr^{3+}, Fe^{3+}, Y^{3+}, La^{3+}
diffusion	$Z_j/D°_j = -0.01443 \text{LUMO}_{Me^{z+}} - 0.04968 R_{Me-O} + 1.70669 \times 10^{-4}\Delta E_{WB} + 0.11201$	0.9565	Li^+, Na^+, K^+, Cs^+, Ag^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Sc^{3+}, Cr^{3+}, Fe^{3+}
adsorption	$\log K_{int,j,k} = -0.33991 \text{LUMO}_{Me^{z+}} + 6.40635 R_{Me-O} - 0.01351\Delta E_{WB} - 18.68482$	0.9726	Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}
cation exchange	$\log K_V = -0.02356 \text{LUMO}_{Me^{z+}} + 1.31521 R_{Me-O} - 0.00642\Delta E_{WB} - 3.42402$	0.9885	K^+, Cs^+, Ag^+, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}

[a] Experimental deprotonation $\log K_a$ values from ref 9; $Me(OH)_{Z(S)}$ solubility product $\log K_{sp}$ from ref 10; metal–EDTA mononuclear complexes $\log K_{11}$ from ref 11; solvation free energy $\Delta G°_{solv}$ from ref 12; $Z_j/D°_j$ for cationic diffusion in aqueous solution from ref 13, where Z_j is the cationic valence; intrinsic sorption constants of divalent metal ions on quartz (α-SiO_2) $\log K_{int,j,k}$ from ref 2; the Vanselow selectivity coefficients $\log K_V$ for binary exchange reactions of sodium–monovalent metal ions and calcium–divalent metal ions on Wyoming montmorillonite (SWy-1) from ref 14.

Traditionally, the ratio of the ionic charge and the size of the metal ion can be used to suggest the deprotonation trends of metal aquo-ions.[9,10] With respect to the stability of metal–ligand complexes, the charge and size of the metal ions as well as the stabilization due to the crystal-field and ligand-field effects are recognized as important factors.[11] Relying on the Born solvation model, the standard Gibbs free energy of ion solvation is conventionally explained as the difference between its potential energy in vacuum and in the continuous dielectric medium.[12] The diffusion of metal ions in electrolyte solutions can be described in terms of the activity gradient and the limiting equivalent ionic conductance of metal ions.[13] To predict the cation-exchange selectivity coefficients, the cation hydration, anion field strength, and hard–soft acid–base (HSAB) models have been proposed.[14]

However, there are several drawbacks in the above conventional theorems in characterizing the aqueous and surface reactions of metal ions. Because of the electron sharing effect, the simple electrostatic model for the deprotonation of metal aquo-ions is unable to rationalize the behavior of metal ions with different electronic configurations. Similarly, to describe the deprotonation trends of metal ions, the metal–ligand complexes must be classified into different groups according to their electronic configurations. In general, the first group consists of metal ions with inert-gas electronic configurations. The second group contains those transition-metal ions that have d^{10} or d^8 configurations. The third group contains transition-metal ions with partially filled d-orbital configurations. Moreover, because of the shortcoming in the continuum dielectric assumption, the solvation free energies obtained from the conventional Born solvation model are quite different from the experimental measurements.

To find suitable modeling predictors to overcome the drawbacks mentioned above, the lowest unoccupied molecular orbital energy of metal ions ($\text{LUMO}_{Me^{z+}}$) together with the Me–O bond length (R_{Me-O}) and water-binding energy (ΔE_{WB}) of monohydrated metal ions are employed in the present work. Here, the LUMO energy and the Me–O bond length can be regarded as the nonsolvation contributions that result from the intrinsic properties of the metal ions. The water-binding energy is responsible for the solvation contribution term. As a result, the general form of the linear model for predicting the thermodynamic constants (Y) of deprotonation, precipitation, complexation, solvation, diffusion, adsorption, and cation-exchange reactions of metal ions can be represented as

$$Y = \alpha \text{LUMO}_{Me^{z+}} + \beta R_{Me-O} + \gamma \Delta E_{WB} + \delta \qquad (5)$$

where the coefficients α, β, γ, and δ reflect different kinds of aqueous and surface reactions of metal ions. The linear predicting models and regression coefficients (r) for the thermodynamic constants of seven chemical reactions of metal ions are listed in Table 2. By using eq 5, the predicted results of seven chemical reactions are also found to have strong correlations with the valence, size, and electron configuration of metal ions, which is consistent with the general chemical rules. Moreover, the regression coefficients (r) for all models are equal to or greater than 0.9547. These results thus demonstrate the feasibility of the preset LFER for predicting the deprotonation, precipitation, complexation, solvation, diffusion, adsorption, and cation-exchange reactions of metal ions.

IV. Conclusions

This work represents the application of the density functional theory method in constructing linear models for predicting essential reactions of metal ions in aquatic and surface systems. Linear free-energy relationships based on the lowest unoccupied molecular orbital energy of metal ions and the Me–O bond

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lengths and water-binding energies of monohydrated metal ions, calculated with the Becke–Perdew–Wang nonlocal density functional method have been derived and were shown to have excellent predictive power.

Supporting Information Available: Lowest unoccupied molecular orbital energy of metal ions ($LUMO_{Me^{z+}}$), Me–O bond lengths ($R_{Me–O}$) in monohydrated metal ions ($Me(H_2O)^{z+}$), and water-binding energies (ΔE_{WB}) of monohydrated metal ions. An example of input data (*DMol*.car and .input files) for the DFT runs. This material is available free of charge via the Internet at http://pubs.acs.org.

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