Estimation of stability constants for metal–ligand complexes containing neutral nitrogen donor atoms with applications to natural organic matter

Yasemin B. Atalay [a], Dominic M. Di Toro [a], Richard F. Carbonaro [b,c,*]

[a] *Department of Civil & Environmental Engineering, University of Delaware, Newark, DE 19716, United States*
[b] *Department of Civil & Environmental Engineering, Manhattan College, Riverdale, NY 10471, United States*
[c] *Mutch Associates, LLC, Ramsey, NJ 07446, United States*

Abstract

Linear free energy relationships (LFERs) were developed for estimating 1:1 metal–ligand stability constants ($\log K_{\mathrm{ML}}$) for small organic molecules containing neutral nitrogen donor atoms. A data set of 44 monodentate and 112 bidentate ligands for six metal ions: Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} was employed to parameterize the LFER equations. Monodentate and bidentate $\log K_{\mathrm{ML}}$ values were adequately described using Irving–Rossotti LFERs previously developed for ligands containing negatively-charged oxygen functional groups. Modifications to the LFER equations were necessary to account for steric hindrances to metal complexation by primary, secondary, and tertiary amines. The resulting LFER equations can be used to estimate $\log K_{\mathrm{ML}}$ values for monodentate and bidentate ligands with neutral nitrogen donor groups where such values do not currently exist in the literature. Comparison of these results to our previous work with negatively-charged oxygen donor atoms reveals that neutral nitrogen functional groups are weaker than their oxygen counterparts for metal ions classified as "hard" on the basis of Hard–Soft Acid–Base (HSAB) theory. For "soft" metals, the opposite is true. These LFERs can be used to incorporate nitrogen functional groups in models for metal ion binding to natural organic matter (NOM).
© 2013 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

Metal ions are important elements in the biogeochemistry of forest and aquatic ecosystems (Driscoll et al., 1994) and many trace metals are required micronutrients for plant and animal life (Marschner, 1995; Reilly, 2004). Industrial processes, mining, fossil fuel combustion and improper waste disposal activities have increased metal loading to the environment and enhanced their bioavailability. The solubility and bioavailability of trace metals are strongly influenced by changes in their aqueous speciation resulting from complexation with a range of inorganic (e.g. OH^-, Cl^-, HCO_3^-) and organic ligands. As a result, equilibrium speciation calculations are often used to provide insight into trace metal cycling and uptake by plants and organisms (Morel and Hering, 1993).

The organic ligands of biogeochemical importance in natural systems are low molecular weight organic acids and humic and fulvic acids which comprise natural organic matter (NOM) (Thurman, 1985). Many of these ligands of interest contain nitrogen atoms (e.g. glycine, alanine, pyruvate) which act as Lewis bases and coordinate metal ions by donating a pair of electrons. The nitrogen-containing functional groups of importance in metal binding are neutral nitrogen donor atoms. These functional groups are partly responsible for the observations of strong metal binding to NOM (Croué et al., 2002; Tipping, 2002; Cabaniss, 2010; Craven et al., 2012). Nitrogen groups may therefore

---

* Corresponding author at: Department of Civil & Environmental Engineering, Manhattan College, Riverdale, NY 10471, United States. Tel.: +1 718 862 7171.
    E-mail address: richard.carbonaro@manhattan.edu (R.F. Carbonaro).

play an important role in biogeochemical cycling of trace metal ions.

Linear free energy relationships (LFERs) are quantitative relationships between chemical reactivity (equilibrium constants or rate constants) and parameters that describe molecular structure and susceptibility to undergo reaction (Johnson, 1975). The original LFER methods, developed for organic chemicals (Wells, 1963), were used to deduce reaction mechanisms, develop synthesis routes, and estimate the biological activity of various organic chemicals (Williams, 2003). LFERs for metal ions have garnered less attention, but relationships have been developed to describe stability constants and kinetic rate constants of metal binding to many ligands (Tucci et al., 1967; Martell and Hancock, 1996).

Several databases of metal–ligand stability constants are publically available including the NIST Standard Reference Database 46 (Martell et al., 2004), and the IUPAC Stability Constants Database (SC-Database) (IUPAC, 2005). The stability constants in these databases are used in geochemical and environmental equilibrium speciation models such as MINEQL+ (Environmental Research Software, 2007) and WHAM (Tipping, 1998; Tipping et al., 2011), and transport codes such as PHREEQC (Parkhurst and Appelo, 1999) and TICKET (Farley et al., 2008, 2011). However, these databases are not comprehensive for all metal–ligand complexes of interest. Filling data gaps via experimental measurement is not practical due to the large effort involved (Dimmock et al., 1995). LFERs may be a good alternative provided they are generally applicable to many metal ions, and are sufficiently accurate in their predictive capabilities.

Recent work by Carbonaro and Di Toro (2007) indicates that stability constants for metal ion complexes with monodentate ligands containing negatively-charged oxygen donor atoms (e.g. acetate, benzoate, phenolate ions) can be estimated using the following equation:

$$\log K_{ML} = \alpha_O \log K_{HL} + \beta_O \qquad (1)$$

where $\log K_{ML}$ is the metal–ligand stability constant, and $\log K_{HL}$ is the proton-ligand stability constant for a monodentate ligand. The value of $\log K_{HL}$ is equivalent to the pK_a of the ligand. The constants α_O and β_O result from linear regression of $\log K_{ML}$ versus $\log K_{HL}$ and were termed the Irving–Rossotti slope and intercept in honor of the discoverers of this LFER (Irving and Rossotti, 1956). Eq. (1) makes no distinction between phenolic, carboxylic or inorganic hydroxide functional groups as they all are suitably estimated by the regression line. LFERs of this type were shown to be valid for 24 metal ions (alkaline earth, first, second, third row transition, post transition metals and some lanthanides and actinides) (Carbonaro and Di Toro, 2007). The intercept (β_O) of all LFERs was nearly zero for all metal ions investigated. Therefore, only one metal-specific parameter (α_O) is required to relate $\log K_{ML}$ and $\log K_{HL}$. Since pK_a values ($\log K_{HL}$) are usually known, Eq. (1) can be used to estimate the stability constants for metal complexes with monodentate ligands containing negatively-charged oxygen donor atoms.

LFERs for estimating the stability constant of bidentate complexes for 20 metal ions have also been developed (Carbonaro et al., 2011). Initially, the Irving–Rossotti monodentate LFER was used to calculate the individual contributions of each binding site of bidentate ligands (Tipping and Hurley, 1992):

$$(\log K_{ML})_{SUM} = \alpha_O \log K_{HL,1} + \alpha_O \log K_{HL,2} \qquad (2)$$

where $K_{HL,1}$ and $K_{HL,2}$ represent the stability constants for protonation of the individual negatively-charged oxygen functional groups and the quantity ($\log K_{ML})_{SUM}$ represents the sum of their contributions. Eq. (2) was shown to systematically underestimate values reported in the NIST Critical database, ($\log K_{ML})_{NIST}$ (Carbonaro et al., 2011). However, the difference between ($\log K_{ML})_{SUM}$ and the 1:1 line increased linearly with increasing values of ($\log K_{ML})_{NIST}$. Also, this difference approaches zero as ($\log K_{ML})_{NIST}$ approaches zero. The systematic bias was eliminated by using a slope-correction, χ_{OO}:

$$(\log K_{ML})_{LFER} = \chi_{OO}(\alpha_O \log K_{HL,1} + \alpha_O \log K_{HL,2}) \qquad (3)$$

Estimated $\log K_{ML}$ values, ($\log K_{ML})_{LFER}$, were accurate to within approximately 0.30 log units. From a chemical perspective, χ_{OO} can be interpreted as a term which provides additional free energy for metal–ligand complexation that arises from the well-known chelate effect (Adamson, 1954; Martell and Hancock, 1996). The subscript "OO" designates that the ring is formed by two oxygen donor atoms. Five and six-membered rings possessed slightly different χ values denoted as χ_{OO}^5 and χ_{OO}^6, respectively.

The monodentate (Eq. (1)) and bidentate (Eq. (3)) LFERs provide new methods for estimating the stability constant ($\log K_{ML}$) of 1:1 metal complexes with ligands containing negatively-charged oxygen donor atoms. Values for α_O, χ_{OO}^5 and χ_{OO}^6 are available for 20 metal ions. Use of the LFER requires knowledge of only the pK_a value(s) of the ligands, and the number of atoms in the chelate ring. The pK_a values of most ligands of interest are known from experimental measurement or can be estimated using computational methods (e.g. SPARC) (Hilal et al., 1996). Therefore, these LFERs can be used quite easily to supplement databases where data gaps are present. Unlike previous LFERs from metal–ligand complexation, parameters for a large number of metal ions are available.

The objective of this work is to develop a LFER framework for estimation of stability constants for metal binding to ligands containing neutral nitrogen donor atoms. The obvious approach is to utilize the same basic formulation that was successful for ligands containing negatively-charged oxygen donor atoms. The LFER equations must be flexible enough to handle mixed Lewis base environments since many bidentate ligands contain one neutral nitrogen and one negatively-charged oxygen donor atom (e.g. glycine). Development of LFER equations for neutral nitrogen donor atoms is complicated because of the need to account for steric interactions, particularly for ligands containing secondary and tertiary amines. Notwithstanding, it is desirable that the LFER parameters are small in number and relatable to the chemical structure and/or properties of the ligand such as chelate ring size and degree of unsaturation of the amine.