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Evaluation of a Log-Normal Distribution First-Order Kinetic Model for Copper(II)-Humic Acid Complex Dissociation

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■ The pseudo-first-order dissociation of copper(II)-humic acid complexes was studied and found to be very heterogeneous with respect to first-order rate constants. A model for heterogeneous kinetics, based on a log-normal distribution of first-order rate constants, is presented and used to describe the dissociation data. The model is discussed in relation to other methods of kinetic data analysis such as discrete multicomponent models and Laplace kinetic spectra. The concept of an observation window for experiments measuring reaction rates in kinetically heterogeneous systems, based on upper and lower limits of acquisition time, was inferred from the response of model parameters to data-set truncation. Data from the nonlabile component of copper(II)-humate dissociation reactions were found to be described well by the log-normal model. Application of this model to published data for nickel(II)-fulvic acid dissociation also resulted in excellent agreement between observed and predicted kinetics. The adjustable parameters of the model were sensitive to changes in experimental conditions, such as reaction temperature or ionic strength, and were interpretable in terms of realistic physicochemical processes.

Introduction

The interactions between metal ions and humic substances are known to be important in many natural environments. In soils and natural waters trace metal ions, such as Cu^{2+} or Pb^{2+} , may exist predominantly in complexes with humic ligands (1, 2). In particular, the importance of nonequilibrium processes in controlling metal ion speciation in the natural environment is becoming increasingly apparent (3-6). Recently, several studies investigating the kinetics of metal ion-humic substance reactions have been reported (7-10). These papers have presented several approaches to resolving the kinetic heterogeneity inherent in such systems.

To date, the methods used to deal with the kinetics of such heterogeneous systems have been concerned with characterizing kinetically resolvable species in terms of a reaction-rate-defining parameter, such as a first-order rate constant. In an early study of the kinetics of iron(III)-fulvic acid complex formation and dissociation, Langford and Khan (11) recognized the need to resolve the dispersion in reaction rates found in such a system. Their data, however, were explained only in terms of simple reaction kinetics, that is, a single complex dissociating by first-order processes.

A more comprehensive approach to resolving heterogeneous metal-humate complex dissociation kinetics was presented by Olson and Shuman (12). They attempted to determine the concentration distribution of kinetically different species with respect to dissociation rate constant. Their method used an approximate Laplace inversion to transform experimentally determined concentration versus time data into a concentration distribution of complexes with respect to $\log k$, where k is the first-order rate constant.

Olson and Shuman's method showed some success in producing "kinetic spectra" for Cu^{2+} -humic substance complex dissociation; however, the second-order approximation used proved susceptible to experimental noise, and continuous distributions of sites were inferred even when discrete sites were present. In addition, since the description of kinetic data obtained was nonparametric, the approach could not be used in conjunction with modeling techniques.

Lavigne et al. (9) used the Laplace transform method to identify hypothetical sites with discrete dissociation rate constants within a mixture of Ni^{2+} -fulvic acid complexes. These discrete parameters were further refined using nonlinear regression analysis. This provided parametric descriptions of heterogeneous kinetics, which facilitated comparisons of data and were amenable to modeling procedures. Discrete rate constants were also invoked by Plankey and Patterson (8) to describe Al^{3+} -fulvic acid complex formation kinetics; graphical methods were used to resolve two kinetically distinguishable components.

Similar approaches are common in the literature dealing with equilibrium binding of heterogeneous ligands, such as humic substances. Another type of approach is, however, possible, that is, assuming a distribution or site abundance function with respect to a common parameter before data analysis and describing the heterogeneous kinetics in terms of this distribution. The most widely known example of this type of approach in literature pertaining to metal ion-humic substance interactions is probably that of Perdue and Lytle (13), who introduced a description of equilibrium copper(II)-humic acid binding based on a log-normal distribution of formation constants.

This paper extends that approach to the kinetics of copper(II)-humate dissociation reactions by introducing a model based on a log-normal distribution of first-order rate constants. The results of applying this model to experimental data are compared with those from application of previously described models for heterogeneous kinetics.

Theory. Development of Model

The fundamental problem to be addressed is that of describing reaction rates from a complex mixture of an unknown number of ligands, having unknown concentrations and metal complex dissociation rate constants.

Reaction of a mixture of discrete species with different reaction rates to form a common product has been used extensively in analytical chemistry to quantify the individual components in a well-defined mixture (14). In such a case, the rate constants are generally already known and the individual species concentrations determined via multiple linear regression analysis of product concentration versus time data (14). Similar competing-ligand-induced dissociation reactions have been used as a method of observing dissociation from heterogeneous ligands (9, 12). Formation of a common product MA from simultaneous dissociation of n discrete complexes, ML_1 to ML_n , may be expressed as

$$\sum_{i=1}^n \text{ML}_i + n\text{A} \rightleftharpoons n\text{MA} + \sum_{i=1}^n \text{L}_i \quad (1)$$

The integrated form of the equation describing time-dependent behavior for reaction 1 is given by

$$[\text{MA}]_t = [\text{MA}]_0 + \sum_{i=1}^n [\text{ML}_i]_0 (1 - \exp(-k_i t)) \quad (2)$$

where k_i is the first-order rate constant for dissociation of complex ML_i ; $[\text{MA}]_t$ is the concentration of MA at time t ; $[\text{MA}]_0$ is the concentration of MA at the experimental time zero and includes the contribution from reactions which occur during mixing time; $[\text{ML}_1]_0, \dots, [\text{ML}_n]_0$ are the initial concentrations of (hypothetical) complexes $\text{ML}_1, \dots, \text{ML}_n$; and k_1, \dots, k_n are first-order dissociation rate constants for complexes $\text{ML}_1, \dots, \text{ML}_n$.

Equation 2 may be applied to kinetic data by treating all $[\text{ML}_i]_0$ and k_i as adjustable parameters (9) or by defining a set of fixed k_i and estimating $[\text{ML}_i]_0$ values using multiple linear regression (10, 14).

If complex heterogeneity is such that sites form a continuous distribution with respect to $\log k_i$ values, the summation may be replaced with an integral:

$$[\text{MA}]_t = [\text{MA}]_0 + \int_{-\infty}^{+\infty} f(k)(1 - \exp(-kt)) dk \quad (3)$$

where $f(k)$ (or $f(\ln k)$) is a function defining the concentration distribution of complexes ML_i with respect to k (or $\ln k$).

The method for estimating the distribution function (7, 12) may be summarized by

$$C_{\text{ML}}(t) = S \int_{-\infty}^{+\infty} H(k, t) e^{-kt} d \ln k \quad (4)$$

where $C_{\text{ML}}(t) = \sum_{i=1}^n [\text{ML}_i]_t$. The distribution function $H(k, t)$ may be approximated by

$$H(k, t) = \frac{\partial^2 C_{\text{ML}}(t)}{\partial (\ln t)^2} - \frac{\partial C_{\text{ML}}(t)}{\partial (\ln t)} \quad (5)$$

and

$$S = 4C_{\text{ML}}(t) / \sum_{i=1}^n [\text{ML}_i]_0 \quad (6)$$

Alternatively, the form of the distribution describing the dispersion in rate constants may be assumed a priori. Albery and co-workers (15) presented such an approach to model heterogeneous kinetics of charge decay from photosensitive semiconductors, assuming a simple Gaussian distribution in activation energy corresponding to a Gaussian distribution in $\ln k$. Their model (15) may be summarized by

$$\frac{C_{\text{ML}}(t)}{C_{\text{ML}}(0)} = \frac{\int_{-\infty}^{+\infty} \exp(-x^2) \exp[-\tau \exp(\gamma x)] dx}{\int_{-\infty}^{+\infty} \exp(-x^2) dx} \quad (7)$$

where $\exp(-x^2)$ defines the Gaussian distribution; τ is dimensionless time ($\tau = \bar{k}t$, where \bar{k} is the mean rate constant; and γ describes the spread of the distribution ($\gamma = 0$: no dispersion in $\ln k$).

It is proposed that a similar distribution of first-order constants may be operative for dissociation of Cu^{2+} -HA complexes, though the dispersion in rate constants may be due to factors other than differences in activation energies. Since, however, the mean and standard deviation

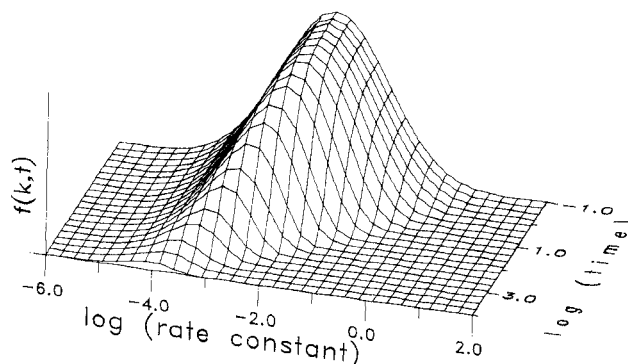


Figure 1. Decay of a hypothetical population of dissociating complexes log-normally distributed with respect to first-order rate constant: mean $\log k$, $\mu = 2.0$, and $\sigma = 1.0$; adapted from ref 15.

of the standard normal distribution are more generally understood parameters than \bar{k} and γ in this model, a different formulation is proposed. Defining $\kappa = \ln k$

$$[\text{MA}]_t = [\text{MA}]_0 + \frac{\text{ML}_{\text{obs}}}{\sigma\sqrt{2\pi}} \int_{-\infty}^{+\infty} \exp\left[-\frac{1}{2}\left(\frac{\kappa - \mu}{\sigma}\right)^2\right] (1 - \exp(-e^{\kappa}t)) d\kappa \quad (8)$$

where μ and σ are the mean and standard deviation, respectively, of the distribution in $\ln k$ and ML_{obs} is the "observed" concentration of sites, such that

$$\text{ML}_{\text{obs}} = |[\text{ML}]_0 - [\text{ML}]_{\infty}| \quad (9)$$

since the integral of the standard normal distribution is equal to unity. In this work, μ , σ , and ML_{obs} were treated as adjustable parameters when this equation was fitted to kinetic data. Figure 1 shows the decay in such a hypothetical population of copper(II)-humate complexes as the dissociation reaction proceeds.

Materials and Methods

Experiments were conducted using the International Humic Substances Society (IHSS) reference humic acid extracted from the A_h horizon of the Summit Hill tussock grassland soil, Banks Peninsula, New Zealand, and humic acid extracted from Waimari peat, Canterbury, New Zealand. Extraction and purification of these materials followed the method adopted by the IHSS for soil humic acids (16). 4-(2-Pyridylazo)resorcinol, (PAR; Sigma) was obtained as the free acid and used without further purification; stock solutions were prepared by dissolving PAR in an equimolar amount of NaOH solution. All water used was purified to a resistivity of 18.3 MΩ cm in a Barnstead Nanopure system. All other chemicals used were analytical-grade. Glassware and plasticware was always acid-washed (1 mol L⁻¹ HNO₃, ≥24 h) and rinsed thoroughly with purified water before use.

Experiments were performed using a pseudo-stopped-flow spectrophotometric technique adapted from Shuman et al. (7). This method uses an excess of the metallochromic ligand PAR to induce pseudo-first-order dissociation of Cu^{2+} from its complexes with humic ligands. Formation of the Cu-PAR complex is monitored spectrophotometrically as a function of reaction time.

Solutions of the sodium salts of Summit Hill humic acid (SHA; 49.5% carbon) or Waimari peat humic acid (WHA; 52.7% carbon) (0.05 g L⁻¹) and Cu^{2+} (7.87 μmol L⁻¹) were prepared such that $[\text{NaNO}_3] = 0.10 \text{ mol L}^{-1}$ and pH = 6.00. These solutions were allowed to equilibrate for 24 h at 20 °C. A PAR solution (0.5 mmol L⁻¹, pH 6.00, $[\text{NaNO}_3] = 0.10 \text{ mol L}^{-1}$) was also prepared. These two solutions were

Table I. Fitted Parameters Derived from Application of Equation 2 ($n = 3$) to Cu^{2+} -HA Dissociation Data^a

	complex				
	Cu-SHA 20 °C	Cu-SHA 30 °C	Cu-SHA 40 °C	Cu-WHA 20 °C	Cu-SHA (truncated) 20 °C
$[\text{CuL}_1]_0, \mu\text{mol L}^{-1}$	0.60 ± 0.03	0.70 ± 0.04	0.63 ± 0.01	0.54 ± 0.01	0.35 ± 0.07
$\log k_1$	-0.93 ± 0.03	-0.88 ± 0.01	-0.80 ± 0.03	-0.96 ± 0.02	-0.71 ± 0.05
$[\text{CuL}_2]_0, \mu\text{mol L}^{-1}$	0.95 ± 0.02	1.04 ± 0.02	1.11 ± 0.01	0.79 ± 0.02	0.69 ± 0.03
$\log k_2$	-1.96 ± 0.04	-1.82 ± 0.03	-1.65 ± 0.02	-2.00 ± 0.02	-1.5 ± 0.1
$[\text{CuL}_3]_0, \mu\text{mol L}^{-1}$	0.62 ± 0.03	0.66 ± 0.02	0.70 ± 0.02	0.69 ± 0.03	0.87 ± 0.09
$\log k_3$	-3.05 ± 0.04	-2.85 ± 0.06	-2.55 ± 0.02	-3.11 ± 0.01	-2.39 ± 0.07
$\sum_{i=1}^3 [\text{CuL}_i]_0, \mu\text{mol L}^{-1}$	2.18 ± 0.06	2.40 ± 0.06	2.43 ± 0.02	2.02 ± 0.04	1.87 ± 0.04
minimum r^2 (%)	99.95	99.96	99.98	99.96	99.93

^a Mean values \pm standard errors for regressions of replicate experiments.

drawn into identical syringes and introduced into the reaction chamber by simultaneous injection via a simple T-junction mixing device. Kinetic runs were started manually as the flow stopped. Calculations using published constants for Cu^{2+} -PAR formation and PAR protonation (17) indicated that the predominant copper(II)-PAR species at pH 6 and ionic strength 0.1 mol L^{-1} was CuPAR^+ . The effective molar absorptivity of the copper(II)-PAR complexes present was determined by measuring the absorbance of solutions of Cu^{2+} and PAR at the concentrations used in dissociation experiments.

Spectrophotometric data acquisition at 510 nm used a Philips PU8700 instrument linked to a Philips P3105 IBM XT compatible PC. Measurements were performed at 20, 30, and 40 °C for Cu-SHA and 20 °C for Cu-WHA using a thermostated cell block; a semimicroflow cell with 1-cm path length served as the reaction chamber.

Numerical Methods

The Philips spectrophotometer produced binary percent transmission data which was equally spaced with respect to time. A simple BASIC program was written to convert these data to absorbance, with approximately equal log (time) intervals; data sets contained ca. 50 data pairs. Model fitting according to eq 2, with one to four discrete sites, used the multidimensional simplex method of Nelder and Mead (18) to minimize a residual sum of squares term by optimizing $[\text{ML}_i]_0$ and $\log k_i$ parameter sets (optimization used $\log [\text{ML}_i]_0$ values to obviate negative solutions). Generation of discrete kinetic spectra by multiple linear regression followed criteria for component selection described by Cabaniss (10) and was performed using MINITAB (19). The kinetic spectrum method of Shuman and co-workers was implemented by smoothing $\sum [\text{ML}_i]_t$ versus $\ln t$ data using high-order polynomials as suggested by Lavigne et al. (9) and calculating first and second derivatives analytically from polynomial coefficients. The Nelder-Mead optimization algorithm was also used to fit data to the log-normal model (eq 8); integrals were solved numerically using the computationally efficient Romberg method (20, 21). Optimization programs were written in FORTRAN using adaptations of listings presented by Press et al. (20); source codes were compiled and run on a DEC VAX minicomputer.

Results and Discussion

Dissociation of Cu^{2+} from SHA and WHA was qualitatively similar. Dissociation of Cu-SHA as a function of $\ln t$ is presented in Figure 2 for experiments performed at 20, 30, and 40 °C, showing an expected increase in dissociation rate with increasing temperature. Variability in t_0 absorbance readings was low, despite the estimated

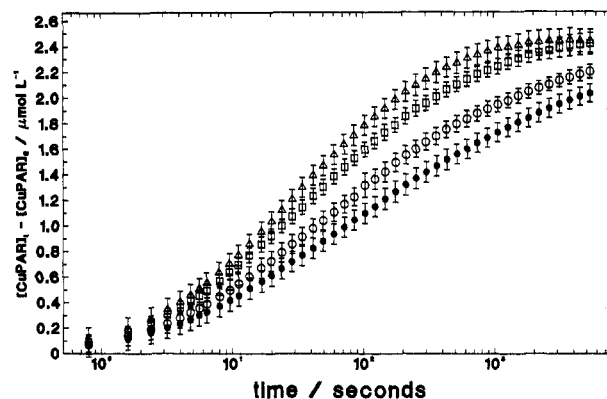


Figure 2. CuPAR formation as a function of time for dissociation of Cu-SHA at 20 °C (○), 30 °C (□), and 40 °C (Δ) and Cu-WHA at 20 °C (●). Error bars are standard errors of means for replicate experiments.

± 0.5 -s mixing time uncertainty. Approximately 56–63% of the Cu^{2+} -HA complexes dissociated within the experimental mixing time, 26–31% of Cu^{2+} -HA complexes dissociated at a rate able to be observed directly, and 10–14% of Cu^{2+} -HA did not dissociate within the time scale (ca. 90 min) of kinetic runs, despite an apparent equilibrium absorbance observed in some experiments (Figure 2). This apparently nonreactive humate-bound copper was attributed to complexes more stable than CuPAR . A value for the molar absorptivity of CuPAR^+ of 40300 ± 400 was found under these experimental conditions.

Discrete Multicomponent Models. The discrete component kinetic model with a single site did not give an acceptable description of Cu^{2+} -HA complex dissociation kinetics (Figure 3). This was not surprising, given that apparent half-lives for the observed reactions showed a consistent increase with increasing reaction time. The discrete multicomponent kinetic model (eq 2) did, however, provide an acceptable ($R^2 \geq 99.3\%$) description of $[\text{CuPAR}]$ versus t data with at least two components. Successful optimization was also achieved using three discrete components, whereas a four-component model seldom converged to a unique solution. The adjustable parameters in the discrete multicomponent models appear to be sensitive to changes in experimental conditions; however, the empirical nature of the model and the large number of adjustable parameters make comparisons difficult.

Application of discrete models to data sets with different acquisition times (10 and 90 min) emphasized the operational nature of the refined parameters and suggested a dependence on an "observation window" analogous to that described for equilibrium binding of metal ions to humic substances (22). Table I summarizes fitted parameters from application of a three-component model to kinetic

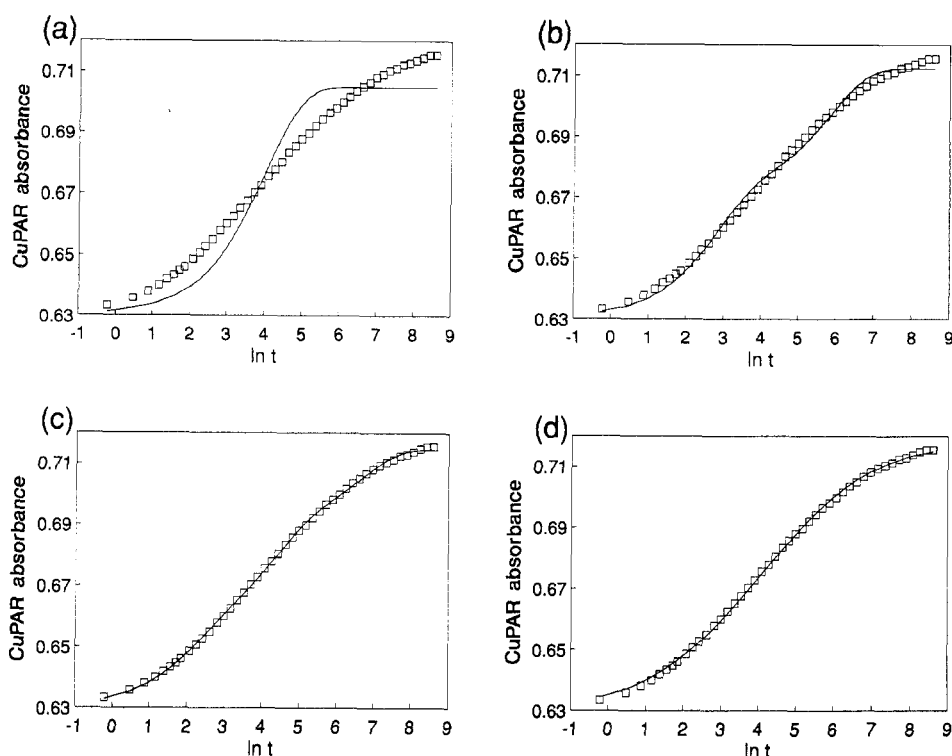


Figure 3. Observed (\square) and predicted (—) CuPAR formation as a function of time for Cu-SHA dissociation, 20 °C, using eq 2 for (a) $n = 1$, (b) $n = 2$, and (c) $n = 3$ and eq 8 for (d).

data sets; truncated data sets (ca. 600 s) contained similar numbers of data pairs and were also equally spaced with respect to log (time). Analysis of Cu^{2+} -SHA complex dissociation data at 20 °C from truncated and untruncated data sets using a three-component model (Table I) reveals smaller $[\text{CuL}_i]_0$ values and more positive log k_i . This is consistent with the lesser degree of reaction completion for the truncated data and the empirical nature of the fitted parameters for this model. If the fitted parameters had any physicochemical meaning, it might have been expected that $[\text{CuL}_i]_0$ and log k_i for the faster reacting sites would have remained unchanged relative to those found for the untruncated data.

Discrete Kinetic Spectra. The discrete kinetic spectrum procedure was able to describe Cu^{2+} -HA dissociation data very well, as found previously (10). In general, six to seven significant components were found for individual runs (Figure 4); however, there was poor reproducibility between replicates with respect to the concentration of components within a particular log k interval. In general, discrete kinetic spectra implied a broad, unimodal concentration distribution of log k_i values, although an obvious second maximum occurred at more negative log k for less complete reactions (e.g., those for Cu-SHA at 20 °C; Figure 4).

Laplace Kinetic Spectra. Laplace spectra (Figure 5) also indicated very broad concentration distributions with respect to the rate constant for Cu^{2+} -HA complex dissociation. For reactions having flatter long-time absorbance readings (e.g., Cu-SHA dissociation at 30 and 40 °C), these distributions tended to be unimodal, with peak widths at half-height much greater than the theoretical value of $1.697 \ln k$ calculated (12) for a single component. Multiple peaks were observed for less complete reactions (Figure 5), but these were poorly resolved and replication of spectra between individual runs was poor. Distributions implied by both this method and discrete kinetic spectra were similar.

Log-Normal Kinetic Model. In many cases, the preceding methods of data analysis (discrete multicomponent

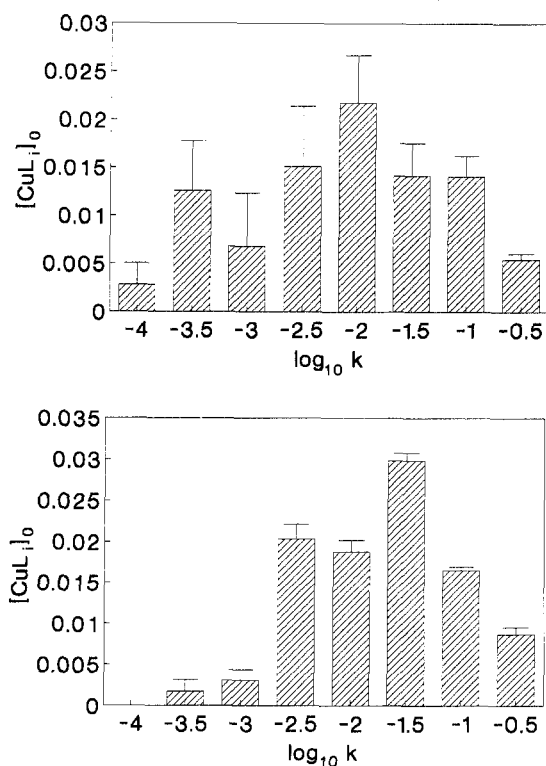


Figure 4. Discrete kinetic spectra for Cu-SHA dissociation at (a, top) 20 and (b, bottom) 40 °C; means \pm standard errors for replicate experiments.

regression, discrete kinetic spectra, Laplace spectra) imply a simple, and in some cases unimodal, concentration distribution of components with respect to log k . This was considered to provide some justification for the application of a model assuming a symmetrical, unimodal distribution of components with respect to dissociation rate constant. Application of a model with a log-normal distribution of first-order rate constants (eq 8) to kinetic data provided

Table II. Fitted Parameters Derived from Application of Equation 8 to Cu²⁺-HA Dissociation Kinetics Data^a

	complex				
	Cu-SHA 20 °C	Cu-SHA 30 °C	Cu-SHA 40 °C	Cu-WHA 20 °C	Cu-SHA (truncated) 20 °C
ML _{obs} , μmol L ⁻¹	2.23 ± 0.02	2.36 ± 0.02	2.38 ± 0.01	2.15 ± 0.001	2.11 ± 0.04
mean ln <i>k</i> , μ	-4.66 ± 0.03	-4.25 ± 0.01	-3.92 ± 0.02	-5.09 ± 0.03	-4.46 ± 0.05
SD ln <i>k</i> , σ	2.11 ± 0.01	1.93 ± 0.03	1.65 ± 0.01	2.39 ± 0.03	1.94 ± 0.01
minimum <i>r</i> ² , %	99.92	99.94	99.98	99.89	99.90

^a Means ± standard errors for regressions on replicate experiments.

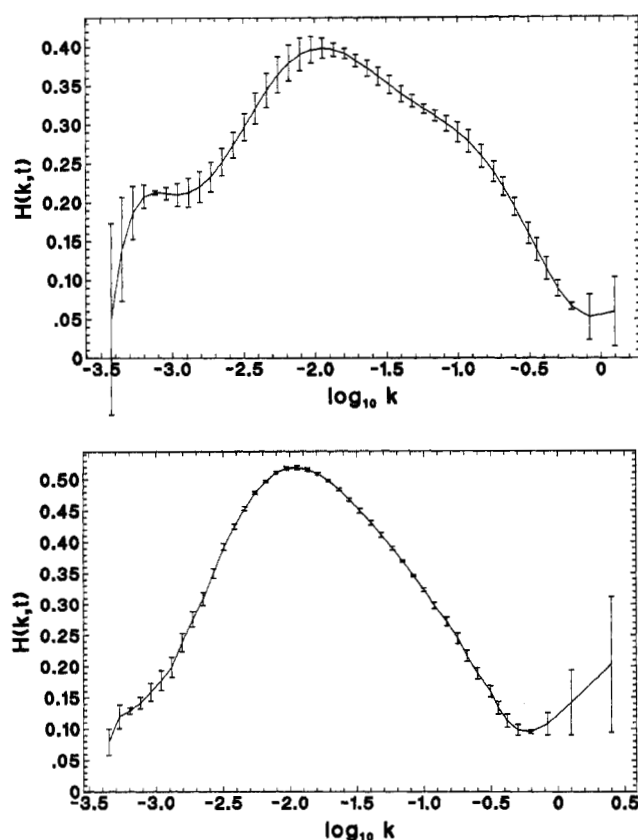


Figure 5. Laplace kinetic spectra for Cu-SHA dissociation at (a, top) 20 and (b, bottom) 40 °C; mean spectra ± standard errors for replicate experiments.

excellent agreement between observed and predicted dissociation ($R^2 \geq 99.89\%$), even where previous methods of analysis had implied multimodal distributions with respect to ln *k*. The model tended to slightly underestimate dissociation rates at short times and overestimate at long times; however, agreement between observed and predicted kinetics was comparable to that achieved by the three discrete component model, having six adjustable parameters (Figure 3), although the log-normal model contained only three fitting parameters. The three-site (Table I) and log-normal (Table II) models also gave similar estimates for the total concentration of sites dissociating during observation times. Refined parameters were dependent on data acquisition time (Table II), as already mentioned for the discrete multicomponent models. The observed increase in Cu-SHA dissociation rate with increasing temperature, and faster dissociation from Cu-SHA compared with Cu-WHA, were reflected in the estimates for the mean rate constants (Table II). Decreasing estimates of the spread in ln *k*, σ, as temperature increased were consistent with the expected greater sensitivity of sites with small *k*_i (large *E*_a) to temperature increase, re-

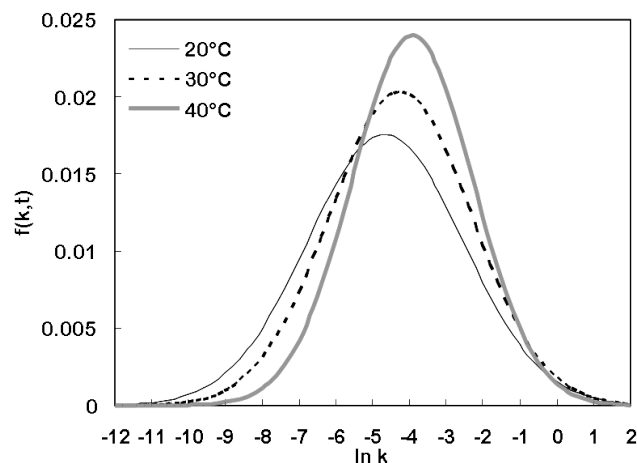


Figure 6. Changes in the hypothetical distribution of Cu-SHA complexes with respect to dissociation rate constant (eq 8) with changing reaction temperature.

sulting in a narrower spread of ln *k* values (Figure 6).

It would be tempting to use the relationship between mean ln *k* and temperature to estimate a "mean activation energy" for the reaction. This was not attempted for the following reason. The model describes kinetics on a macroscopic basis only; it is impossible to ascertain, on a microscopic scale, whether the physical set of Cu²⁺-HA complexes having ln *k* = μ at one temperature also have ln *k* = μ at other temperatures.

Implicit to all the preceding methods of data analysis is the assumption of first-order behavior for Cu²⁺-HA complex dissociation. It is considered that the large molar excess of PAR over Cu²⁺ resulted in pseudo-first-order conditions being fulfilled; other work (7, 12) has shown that the copper-organic complex dissociation rate is independent of PAR concentration, even with PAR in only 3-fold excess over Cu²⁺. Hering and Morel (4) found that both adjunctive (bimolecular) and disjunctive (unimolecular) processes were operative for Cu²⁺-HA dissociation at low copper/HA ratios (ca. 4 μmol of Cu/g of HA). These workers also found (4) that at higher Cu/HA ratios, such as those dictated by the experimental methods used here (ca. 160 μmol of Cu/g of HA), the disjunctive mechanism for Cu²⁺-HA dissociation predominated, and thus it is most likely that these reactions were also first order on a microscopic basis.

The log-normal model is used in this work to describe only a proportion of copper(II)-humate complex dissociation kinetics, due to the nature of experiments and the large proportion of very labile complexes present. Evidence that the model is appropriate for describing more complete data sets is obtained by its application to data presented by Cabaniss (10) for Ni²⁺-fulvic acid complex dissociation (ref 10; Table III). Zero-time values for [Ni(PAR)₂] were included in these data sets (i.e., [Ni(PAR)₂] = 0 at *t* = 0). The log-normal model (reformu-

Table III. Fitted Parameters Derived from Application of Log-Normal Kinetic Model to Ni²⁺-Fulvic Acid Dissociation Kinetics Data^a

	experiment						
	pNa 1.0	pNa 1.5	pNa 2.0	pNa 2.4	pNa 2.7(a)	pNa 2.7(b)	pNa 2.7(c)
ML _{obs} , μmol L ⁻¹	4.909	4.912	4.953	4.971	4.949	4.870	4.821
μ	-2.326	-2.79	-3.197	-3.363	-3.699	-3.982	-4.137
σ	1.183	1.152	1.069	1.114	0.883	0.795	0.918
r ² , %	99.78	99.90	99.93	99.90	99.97	99.94	99.95

^a See ref 10, Table III, for experimental details.

lating eq 8 to describe exponential decay) described these data very well (Table III), even though it was found that four discrete components (one aquo-Ni²⁺ and three Ni²⁺-FA species) were required to adequately represent the data (10). Inspection of the fitted parameters (Table III) reveals that both μ and σ decrease with decreasing ionic strength, while the predicted total concentration of dissociating Ni²⁺ species (ML_{obs}) remained approximately constant and equal to the actual Ni²⁺ concentration. These trends correspond to slower dissociation of Ni²⁺-FA complexes at lower ionic strength, a conclusion consistent with analysis of these data by other methods (10). For the same reasons as for temperature dependence, however, it is not possible to identify changes in concentration of individual species on a microscopic basis in this, or any, hypothetical discrete or continuous site distribution.

The effect of changing Ni/FA ratio on Ni²⁺-FA dissociation rate is also in partial agreement with that found by Cabaniss (10). Decreasing initial Ni/FA ratio decreased overall Ni²⁺-FA dissociation rate, revealed in decreasing estimates of μ (Table III); no obvious trend was evident for σ values. Such an observation is expected for complexes with ligands which are heterogeneous with respect to binding affinity, if more thermodynamically stable complexes also dissociate more slowly. The changes in μ suggest an overall shift in the distribution of sites in $\ln k$ with respect to changing Ni/FA ratio rather than the skewing of the log k distribution suggested by discrete kinetic spectrum analysis (10).

In the application of the log-normal model to Cabaniss' data, reaction rate heterogeneity introduced by dissociation of Ni(H₂O)₆²⁺ and kinetically indistinguishable species is incorporated into the distribution in $\ln k$. A more physicochemically realistic model can be formulated to include terms for the initial concentration, and dissociation rate constant, for aquo-metal species in addition to the log-normal distribution in $\ln k$ for metal-humate species. Attempts to apply such a modified model to Cabaniss' data (10) in this laboratory were thwarted by two factors: (i) the absence in Cabaniss' paper of Ni(H₂O)₆²⁺ dissociation rate constants for all experimental conditions and (ii) a degree of instability that was introduced into the regression procedure by adding a further adjustable parameter ([Ni(H₂O)₆²⁺]₀) to a model which already fit the data very well (Table III). These problems could obviously be circumvented by making separate measurements of Ni(H₂O)₆²⁺ concentration in Ni²⁺-FA systems before reaction with PAR and measuring PAR-induced Ni(H₂O)₆²⁺ dissociation rate constants in the absence of FA.

It is clear that the log-normal kinetic model provides a good description of heterogeneous kinetics on a empirical, macroscopic basis, comparable with that achieved using discrete multicomponent models with a greater number of adjustable parameters. However, the model gives no specific information regarding chemical reaction mechanisms. The assumption of first-order behavior is justified

by the experimental procedures used, but it may be questionable whether such an assumption is true for natural systems without supporting evidence. It has been shown, however, that this model can provide estimates of mean and variability in rate constants consistent with a physicochemical interpretation of differences in kinetic behavior due to changing conditions (such as temperature) for Cu²⁺-HA complex dissociation reactions. It is considered likely that the log-normal kinetic model will provide a useful tool for succinct parametric comparisons of changes in kinetic behavior for kinetically heterogeneous systems.

Registry No. Cu, 7440-50-8; Ni, 7440-02-0.

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Dissolution of Monoaromatic Hydrocarbons into Groundwater from Gasoline-Oxygenate Mixtures

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■ The effects of the "oxygenate" additives methanol and methyl *tert*-butyl ether (MTBE) on the aqueous solubility of benzene, toluene, ethylbenzene, and xylenes (BTEX) from gasoline were evaluated through equilibrium batch experiments. For a gasoline:water ratio of 1:10 (v/v), up to 15% MTBE or up to 85% methanol in gasoline produced no enhanced BTEX solubility. However, at higher gasoline:water ratios, aqueous methanol concentrations above 10% enhanced BTEX solubility. The initial methanol content of the gasoline and the equilibrating gasoline- to water-phase ratio controlled the aqueous methanol concentration. Partitioning theory and the experimental results were used to calculate aqueous benzene and methanol concentrations in successive batches of fresh groundwater equilibrating with the fuel and subsequent residuals. These successive batches simulated formation of a plume of contaminated groundwater. The front of the plume generated from high-methanol gasoline equilibrating with groundwater at a gasoline:water ratio of more than 1 had high methanol content and elevated BTEX concentrations. Thus, releases of high-methanol fuels could have a more serious, initial impact on groundwater than do releases of methanol-free gasoline.

Introduction

Monoaromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes (termed BTEX as a group) are the most water-soluble and mobile and among the most potentially harmful hydrocarbons found in gasoline. Their concentrations in groundwater in contact with gasoline can be estimated, within a factor of 2 (1-3), from the aqueous solubility of the pure component, its mole fraction in the gasoline, in accordance with Raoult's law (assuming gasoline is an ideal solution whose components have unit activity coefficients):

$$C_w^i = s^i x_g^i \quad (1)$$

where C_w^i is the equilibrium concentration of component i in the water phase, s^i is the solubility of pure component i in water, and x_g^i is the mole fraction of component i in the gasoline. Benzene has a "solubility" (s^i) of ~1800 mg/L, but since it makes up less than 5% (v/v; $\approx x_g^i$) of most gasolines, the benzene concentration in waters affected by gasoline should be less than 90 mg/L. This is still 4 orders of magnitude above regulatory action levels, which are typically near 5 μ g/L. This solubility could be dramatically increased if a water-soluble cosolvent is present in the gasoline (4, 5).

Oxygen-containing organic compounds ("oxygenates"), such as ethers and alcohols, are common additives to gasoline (6) and are potential cosolvents. Fuels with high oxygenate content will contain less BTEX than non-oxygenated fuels. Applying eq 1, a decrease in the BTEX content of the gasoline would decrease the BTEX concentration in impacted groundwater. However, the well-documented cosolvency effect (5, 7-13) would increase BTEX solubility by increasing the term s^i . For unexpectedly high BTEX concentrations to appear in groundwater, it is not sufficient that the solubility of BTEX simply be higher than in systems with no cosolvent present. Enough BTEX must be available to partition into the groundwater at high concentrations along with the cosolvent. Here, this potential enhancement of BTEX solubility is considered for methanol and MTBE in gasoline.

Theory

Partitioning Theory. This paper treats the dissolution of BTEX and oxygenates in gasoline-water systems as attaining an equilibrium partitioning between aqueous and organic phases of specified volumes or volume ratios, an approach outlined in refs 14 and 15. This approach is well-suited for spill situations where the gasoline- to aqueous-phase ratio may be site-specific.

A mass balance expression for the equilibrium partitioning of each component (e.g., benzene) in a two-phase system of gasoline and water is

$$y_g^b V_g \rho^b = c_g^b V_g + c_w^b V_w \quad (2)$$

where y_g^b is the volume fraction of benzene in the gasoline, V_g is the initial volume of the gasoline (m^3), ρ^b is the density of benzene (g/m^3), c_g^b and c_w^b are the equilibrium concentrations of benzene in the gasoline and in the water phase, respectively (g/m^3), and V_g and V_w are the volumes of the gasoline phase and the water phase, respectively, at equilibrium (m^3). The left-hand side of eq 2 represents the total mass of benzene, and the right-hand side expresses the distribution of this mass between the gasoline and the water phases.

The distribution of benzene between the two phases can be described in terms of a gasoline-water partitioning coefficient, K_{gw}^b , where

$$K_{gw}^b = c_g^b / c_w^b \quad (3)$$

We will assume that (1) applies; then

$$c_w^b = x_g^b s^b \quad (4)$$

where x_g^b is the mole fraction of benzene in gasoline and

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