Understand the Extraordinary Ionic Reactivity of Aqueous Nanoparticles

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ABSTRACT: Nanoparticles (NPs) are generally believed to derive their high reactivity from the inherently large specific surface area. Here we show that this is just the trivial part of a more involved picture. Nanoparticles that carry electric charge are able to generate chemical reaction rates that are even substantially larger than those for similar molecular reactants. This is achieved by Boltzmann accumulation of ionic reactants and the Debye acceleration of their transport. The ensuing unique reactivity features are general for all types of nanoparticles but most prominent for soft ones that exploit the accelerating mechanisms on a 3D level. These features have great potential for exploitation in the catalysis of ionic reactions: the reactivity of sites can be enhanced by increasing the indifferent charge density in the NP body.

INTRODUCTION

Knowledge of the reactivity of natural or synthetic nanoparticles (NPs) towards molecular and ionic reactants is fundamental to sorting out questions about their environmental fate and their impact on ecotoxicology and human health. It is also a prerequisite in their purposeful use e.g., in the intelligent design of smart nanoparticles with tailored functionality that also a prerequisite in their purposeful use e.g., in the intelligent design of smart nanoparticles with tailored functionality that are loose and fragmentary. Here we propose a comprehensive approach that encompasses the unique physicochemical characteristics of the nanoparticulate regime. The focus will be on ionic chemical reactions of the soft aqueous nanoparticle that is ion- and water-permeable. Such a particle generally carries electric charge and reactive sites, both distributed over its entire volume (3D).

The typical situation of a reactive nanoparticle dispersed in a medium with dissolved reactant ions is shown in Figure 1. The reactive sites are spatially confined to the particle body that is at a potential different from that in the bulk medium. Evidently, the rate of diffusional reactant transport from the bulk medium to the reactive sites decreases on going from the molecular to the nanoparticulate to the colloidal case, simply as a result of the increasing distances involved. However, the local concentrations of ions and reactants inside the particle body can be very different from those in the bulk medium, especially for ionic reactants. As a result, the reactions of NPs with small ions may be accelerated and even become faster than those for similar nonparticulate molecular reactants. Here we shall explain the physicochemical basis for this effect.

Consider for example the association of an aqueous ionic reactant R^z_0 with a reactive group S inside a negatively charged NP body. The rate of association of R^z_0 with the reactive sites, S, as compared to the reaction with individual site molecules (Figure 1a) depends on the relative magnitudes of two primary effects. First, the rate of diffusive reactant supply is lowered (cf.
fast reactions of small ions with the charged nanoparticulate body and the bulk medium. In steps 3 and 4 in Figure 2 may be interrelated with the kinetics involved and identify the conditions under which NPs exhibit electrostatic and chemical processes may run in parallel and be applied on colloidal and larger scales: in the NP domain, that is more comprehensive than conventional approaches. In this respect, nanoparticles call for a physicochemical approach.

The schematic Eigen-type mechanism for the detailed steps involved in the overall association of Raq with nanoparticulate S is shown in Figure 2. The overall reaction rate depends on the relative magnitudes of the convergent reactant diffusion, rate of chemical bond formation with the reactive NP sites, and impact of the electric field within and outside the particle body. Fairly fast reactions of small ions with specific sites within an NP (steps 3 and 4 in Figure 2) may be interrelated with the kinetics of their merely electrostatic Boltzmann partitioning between the charged nanoparticulate body and the bulk medium. In this respect, nanoparticles call for a physicochemical approach that is more comprehensive than conventional approaches applied on colloidal and larger scales: in the NP domain, electrostatic and chemical processes may run in parallel and be intimately coupled. Here we outline the theoretical concepts involved and identify the conditions under which NPs exhibit enhanced reactivity. The approach is illustrated by results for metal ion complexation by soft NPs and reactions of charged organic substrates at impermeable NPs.

Figure 1. Schematic representation of a reactant ion (red dot) in (a) a homogeneous solution of small reactive molecules, (b) a reactive nanoparticulate dispersion, and (c) a reactive colloidal dispersion. The blue dots represent reactive sites.

Figure 2. Steps involved in the association of an aqueous reactant ion, Raq, with a spherical nanoparticle containing charged or uncharged reactive sites (S) and charged indifferent sites (−). The +’s denote the extraparticulate part of the counterionic atmosphere. The steps are (1) diffusion of Raq from the bulk solution to the surface of the nanoparticle, (2) incorporation within the particle body as a free hydrated ion, (3) ion pairing of Raq with S, forming Raq+S, and (4) formation/dissociation of a chemical bond, RS, which may include the loss of water of hydration by Raq. Adapted from ref 13.

EXPERIMENTAL SECTION

The method for measuring the Ni(II) complexation parameters and obtaining the experimental values of the Ni/humic acid (HA) association rate constant, kq, followed the same procedure as previously reported for fulvic substances. In brief, the stability of HA complexes with Ni2+ was determined by depletive stripping chronopotentiometry; the kq values were then obtained from the product of the thermodynamic stability constant and the dissociation rate constant, Kkq, where the applicable kq values were obtained from the literature. Humic acids have a radius, r, of ca. 2.3 to 3 nm; detailed analyses of their electrostatic properties, including the applicable coefficient for conductive transport, f, and the Boltzmann accumulation factor, fb, are reported in the literature.15

RESULTS AND DISCUSSION

We shall describe the various processes at a more quantitative level for the case of soft NPs. The electric field of an NP acts to accelerate the convergent diffusion of oppositely charged ions from the medium and determines the extent to which they accumulate within and around the NP body. These two effects may be described by a Debye coefficient for conductive transport toward the NP, f, and a Boltzmann accumulation factor, fb, respectively. The effective f is derived as the integral average of the local f (numerically evaluated on the basis of the nonlinear Poisson–Boltzmann equation over the various binding positions r inside the NP entity, eq 1)

$$f_{\text{el,a}}(r) = \left[ K \int_0^{\infty} u^{-2} \exp\left( -\frac{zQ(u)}{z} \right) du \right]^{-1}$$

where $k^{-1}$ is the conventional Debye screening length, $zQ$ is the valency of the reactant ion, r is the radial position counted from...
the center of the spherical NP. NP, and $y$ is the dimensionless potential defined by $\frac{zFy}{RT}$, where symbols have their usual meaning. The coefficient $f_{\text{el}}$ pertains to the conductive diffusion toward the entire NP volume and includes both the extraparticulate and intraparticulate parts of the counterionic atmosphere. $f_{\text{el}}$ is the integral average of $f_{\text{el}}(r)$ over the NP volume for an assumed preset electric field (i.e., the settling of the field by an excess 1:1 background electrolyte is considered to be complete on the time scale of the accumulation of the target $R_{\text{iq}}^{\text{f}}$). For sufficiently small NPs and/or low ionic strength, the thickness of the extraparticulate counterionic atmosphere is greater than the particle radius. Then the extraparticulate Boltzmann accumulation of counterions, including the reactant ion $R_{\text{iq}}^{\text{f}}$, is significant and should be taken into account in the reaction rate. Examples of extraparticulate divalent reactant ion distributions are shown in Figure 3 for NPs of radii 1 and 2 nm. For $r_p = 1 \text{ nm}$ usually formulated as a chemical reaction rate constant (i.e., per mole of sites $S$),

$$k_{a,p} = \frac{4\pi N_n R_{a} (D_{R} + D_{NP} f_{\text{el}})}{N_S} \left( \frac{m^3}{mol \cdot s} \right)$$

(2)

where $D_R$ and $D_{NP}$ are the diffusion coefficients of the reactant and NP, respectively, and $N_S$ is the number of reactive sites per NP. The rate constant for the formation of RS (step 4 in Figure 2) is generally governed by the inner-sphere dehydration of $R_{aq}^{\text{f}}$ (rate constant, $k_w$) and increases as $f_{\text{el}}$ increases according to

$$k_w = \frac{k_{w} V^{\text{f}}_{\text{el}} N_{Av}}{(m^3 \cdot mol^{-1} \cdot s^{-1})}$$

(3)

where $V^{\text{f}}_{\text{el}}$ is the volume of the precursor outer-sphere ion pair in which the reactant $R_{aq}^{\text{f}}$ still has an intact inner hydration shell. Equations 2 and 3 are generally applicable for highly charged NPs, irrespective of the importance of the extraparticulate countercharge or the nature of the NP (i.e., soft or hard), with $f_{\text{el}}$ and $f_{\text{el}}$ computed for the pertaining electric field and intraparticulate and/or extraparticulate domains in each case (cf. Figure 3). At low charge density, the local electric field around each reactive site must be taken into account.

The nature of the step that is overall rate-limiting (cf. Figure 2) can change with the electric field of the NP or the ionic strength of the bulk medium or the rate of chemical bond formation. The situation in which the reaction rate for the nanoparticulate sites is enhanced as compared to molecular rates generally arises if Boltzmann accumulation in the NP is the faster process. Then the formation of RS takes place in an environment of locally enhanced concentration of $R_{aq}^{\text{f}}$ (with step 4 in Figure 2 being rate-limiting). We highlight that this effect is due to the mere charge on the NP (i.e., it is a truly electrostatic catalytic effect that is independent of the nature and density of reactive sites).

There is a paucity of quantitative data on reaction rates of well-defined NPs. However, the complexation reactions of metal ions by natural NPs, such as humic acid (HA), have been extensively studied over many years. HA has been shown to be soft and permeable, with carboxyl groups as the predominant functional sites and a structural charge density of ca. $-1000 \text{ mol m}^{-3}$.24 Although these natural NPs are rather complicated and heterogeneous, they are crucial in metal speciation and bioavailability in aquatic media. Thus far, the differences between the observed reactivity of HA and that predicted on the basis of molecular concepts have remained unexplained.25 As a typical example, the complexation of Ni(II) by HA ($r_p \approx 3 \text{ nm}$) may be used to illustrate the applicability of the theoretical results presented herein. The experimental values of the Ni/HA association rate constant, $k_a$, are compared with computed values in Table 1. For comparison, we also show the computed rate constant for inner-sphere complexation, $k_{a,p}$, for Ni(II) complexation by a simple carboxylate ligand where the

![Figure 3. Excess density of reactant ions, $R_{aq}^{\text{f}}$, over that in the bulk medium as a function of radial distance, $r$, from the surface of an NP with radius of 1 nm (solid curve) and 2 nm (dashed curve). The ion density is normalized with respect to that at the surface of the NP ($r = r_p$). The charge density of both NPs is $-2000 \text{ mol m}^{-3}$; the ionic strength of the bulk medium is 10 \text{ mol m}^{-3}.

Table 1. Rate Constants Measured for the Association of Ni(II) with Humic Acid, $k_a$ ($m^3 \cdot mol^{-1} \cdot s^{-1}$), as Compared to Computed Values for Different Ionic Strengths ($r_p = 3 \text{ nm}$, Charge Density $= -1000 \text{ mol m}^{-3}$)

<table>
<thead>
<tr>
<th>Ionic Strength (mol m$^{-3}$)</th>
<th>Experimental log $k_a$</th>
<th>Computed $k_{a,p}$</th>
<th>Computed $k_{a}$</th>
<th>Computed simple ligand log $k_{a}$</th>
<th>Computed simple ligand log $k_{a,p}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>2.8</td>
<td>2.5</td>
<td>7.6</td>
<td>1.8</td>
<td>2.0</td>
</tr>
<tr>
<td>10</td>
<td>4.8</td>
<td>4.4</td>
<td>7.8</td>
<td>2.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

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Table 2. Key Features Involved in the Reactivity of Molecules, Nanoparticles, and Colloids

<table>
<thead>
<tr>
<th>small molecular ligand</th>
<th>nanoparticle</th>
<th>colloid</th>
</tr>
</thead>
<tbody>
<tr>
<td>one reactive site</td>
<td>tens to thousands of reactive sites</td>
<td>over thousands of reactive sites</td>
</tr>
<tr>
<td>only external countercharge atmosphere</td>
<td>both extraparticulate and intraparticulate countercharge</td>
<td>only intraparticulate countercharge significant</td>
</tr>
<tr>
<td>Fuoss-Eigen ion pairing</td>
<td>ion distribution via conductive diffusion (Debye) and Boltzmann partitioning</td>
<td>ion distribution via Boltzmann approaching Donnan for ( k_r \rightarrow 1 )</td>
</tr>
<tr>
<td>generally ( k^o ) is overall association rate-limiting</td>
<td>( k^o ) or ( k_a,p ) may be association rate-limiting, depending on the NP charge, particle size, and rate of chemical bond formation</td>
<td>generally ( k_a,p ) is overall association rate-limiting</td>
</tr>
</tbody>
</table>

The electrostatic contribution to the interaction strength is that of a \( 2^+1^- \) ion pair.20

For the well-charged humic NPs, inner-sphere complexation is overall rate-limiting for the slowly dehydrating \( \text{Ni}^{2+} \). The results in Table 1 show that the experimentally determined \( k_a \) is in convincing agreement with the theoretical \( k^o \) (eq 3). Furthermore, this rate is greatly enhanced over that for a true solution of similar individual binding agents. In agreement with the above theory, the ionic strength dependence is quite pronounced, indicating that the enhanced reactivity is a general feature of NPs. It is manifest within a certain window of conditions, including (i) a particle body sufficiently large to accommodate many reactant ions and charge density sufficiently high so that the intraparticulate accumulation of the reactant is substantial and (ii) overall rate-limiting inner-sphere complexation, (i.e., the rate of the limiting step benefits from a local reactant concentration that is greater than that in the bulk medium). These conditions are met for the example case of \( \text{Ni}^{2+} \) complexation by HA examined herein. However, such conditions are not always met for very rapidly dehydrating metal ions such as \( \text{Cu}^{2+} \) and \( \text{Pb}^{2+} \) nor for particle radii beyond a certain \( r_p \) irrespective of the rate-determining step. In such cases, the rate constant for diffusive supply, \( k_{a,p} \), becomes limiting and thus the enhanced \( k^o \) is immaterial in the overall association rate.13 Even then, the acceleration of reactant diffusion may give rise to an enhancement of the overall \( k_a \). This latter effect is likely the predominant mode of \( k_a \) enhancement for impermeable NPs, for which the local accumulation of the reactant is restricted to the extraparticulate zone.

The same concepts as detailed above are applicable to the reactivity of impermeable and core–shell NPs, with an appropriate consideration of the applicable electrostatic terms. For impermeable NPs under the condition \( \kappa_p \ll 1 \), the acceleration of reactant diffusion can be estimated from the surface potential, \( \psi_p \) via \( U^o = \left( \psi_p / \exp(U^o) - 1 \right) \), where the dimensionless electrostatic interaction energy is \( U^o = z_g F \psi_p / RT \). For example, the photochemical degradation rate of positively charged rhodamine B was enhanced by a factor of ca. 2 at negatively charged surface-modified TiO\(_2\) NPs (\( r_p \approx 3 \) nm).27 The surface potential of the modified NPs was 20 to 40 mV more negative than the naked TiO\(_2\), which translates to a computed enhancement factor of 1.5 to 2. Similarly, the increase in peroxidase activity reported at surface-modified iron oxide NPs (\( r_p \approx 40 \) nm)28 is in agreement with that predicted on the basis of the increasingly positive surface charge (e.g., a factor of 1.5 increase in rate upon changing the surface potential from zero to \( +20 \) mV).

The key features involved in particle reactivity for the size spectrum from small ligands to nanoparticles and colloids are summarized in Table 2.

For several values of the dehydration rate constant, \( k_d \), a pronounced maximum is observed for charged NPs, with \( k_a \) values enhanced up to orders of magnitude over their molecular and colloidal counterparts. As the particle size increases over the nanodomain, the evolution of the \( k_a \) curve reflects the transition from a rising part with increasing \( k^o \) (due to an increased local reactant concentration) to a descending part with a still enhanced \( k_{a,p} \) (due to conductive acceleration of the diffusive transport). Eventually the curve merges with that for the simple case of a purely diffusive \( k_{a,p} \) with a slope of \( -2 \) for diffusion into a spherical body (cf. Figure 1). As explained above, the particle size window over which the rate enhancement is in effect and the magnitude thereof depend on the ionic strength of the medium, the NP charge density, the reactant ion valency, and the rate of the chemical bond formation step. At the onset of the NP regime, for \( r_p \) values on the order of 1 nm, the reactivity enhancement over the molecular scale is still modest. This is because there are physical limitations to the accumulation of the reactant inside the NP body, thus the Boltzmann accumulation is effective practically only in the...
extraparticulate counterion atmosphere. Depending on the electric potential of the particle, some of the accumulated reactant ions are located an appreciable distance from the NP surface (Figure 3). A particle radius of 1 nm thus approaches the $\kappa a_p$ limit at which the site reactivity transitions from the traditional discrete molecular approach (Eigen-Fuoss) to the multisite NP case with enhanced activity of reactive ions in the counterionic atmosphere. In turn, the latter case transitions to the more simple case of a larger Donnan-type particle with an effectively constant electric potential with respect to that of the medium.

## OUTLOOK

An obvious application for the exploitation of these NP features is in the catalysis of ionic reactions. Our present theory predicts that NPs carrying reactant sites and many indifferent charge would be efficient catalysts for ionic reactions, irrespective of whether the reactive site itself is charged. Soft NPs offer the greatest potential for such application because of their exploitation of the involved mechanisms on a 3D level; the reactivity of impermeable NPs can also be enhanced by an appropriate modification of their surface charge. In general, the manipulation of NP charge is a powerful tool for optimizing their functionality.8,9,27–30 The present work provides the fundamental basis for understanding and tailoring the reactivity of NPs.

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### Notes

The authors declare no competing financial interest.

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