Kinetic and Thermodynamic Aspects of Adsorption on Silica Nanoparticles. A Pulse Radiolysis Study

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The rate of the reaction of hydrated electron with methyl viologen, MV^{2+}, and tris(2,2′-bipyridyl)ruthenium(II), $Ru(bpy)_3^{2+}$, in the presence of colloidal silica nanoparticles was measured using the pulse radiolysis technique. The decrease in the rate of the reaction upon addition of the particles was used to determine the concentration of free adsorbate in the suspension. The adsorption equilibrium constant obtained for MV^{2+}, $K = (4.7 \pm 0.3) \times 10^5$ M^{-1}, is identical within the experimental error for all the silica particles studied, independent of particle size (4 nm $\leq r \leq$ 10 nm). The maximum density of bound MV^{2+} at saturation was found to be $(1.0 \pm 0.05) \times 10^{-6}$ mol m^{-2}, also independent of particle size. For $Ru(bpy)_3^{2+}$, a significantly smaller equilibrium constant was obtained, $K = (1.3 \pm 0.1) \times 10^5$ M^{-1}, and the highest density of $Ru(bpy)_3^{2+}$ adsorbed on the same particles is smaller by 30%, 0.70×10^{-6} mol m^{-2}. The differences in adsorption parameters between the two adsorbates are attributed to the difference in molecular sizes and thus charge-density distribution within these two molecules. The adsorption equilibrium constants are independent of loading of adsorbate in the range of 50% to 100% coverage. It is emphasized across this study that the "density of binding sites" determined by using different probes might depend on the probe molecule used.

Introduction

Binding of multivalent ions to molecular aggregates, such as micelles, polyelectrolytes, or the surface of colloidal particles has been studied exhaustively. As a result of the adsorption the rate of reaction of the adsorbed ion is often modified from the rate of the ion in the bulk of the solution.[1-6] The rate of reaction between two oppositely charged ions is frequently reduced in these environments due to the reduction in concentration of one of the ions in the bulk of the solution and due to the reversal of the electrostatic interaction between the reactants. Whereas this effect has been extensively reported quantitative information on the adsorption constant, its dependence on particle size and number of ions that adsorb on the particle is scarce. Recently, we used the ions tris(2,2′-bipyridyl)ruthenium(II), $Ru(bpy)_3^{2+}$, and methyl viologen, MV^{2+}, as hole and electron scavengers in order to quantify the early events in the radiolysis of aqueous colloidal silica nanoparticles.[7,8] Prior to their use as probe molecules, however, the interactions with the silica surfaces have to be understood and the adsorption parameters, such as equilibrium constants and number of adsorbate molecules per particle, have to be quantitatively determined. In this report, we utilize the effect of the silica particle charged surface on the kinetics of the reaction of these two ions with hydrated electrons to determine the adsorption parameters.

Calvin and co-workers have measured binding of, $Ru(bpy)_3^{2+}$, on SiO_2 suspension (Nalco 1115) using a flow dialysis method.[9] The number of adsorption sites on 4 nm SiO_2 particle at pH 9.8 has been determined to be ~65. This value is in good agreement with the number of charges, ~60, determined by other methods.[10] Thus, they concluded that one molecule of Ru-$(bpy)_3^{2+}$ associates with a single charge of an ionic site. The corresponding charge density on the silica surface is ~0.18 C m^{-2} or 1.1 charges per nm^2. This value is often used in the

calculation of charge density of similar colloidal suspensions.[11] Using the same brand of silica, Kamat and co-workers estimated the negative charge on each particle utilizing a pulsed laser photolysis method.[12] The rate of quenching of the triplet state of the anionic dye, Rose Bengal, by MV^{2+} was employed as a marker for the concentration of the free quencher in the bulk of the solution. In the absence of SiO_2 colloids the triplet lifetime is significantly shorter than in the presence of the particles since MV^{2+} quenches the triplet excited state via a diffusion-controlled reaction. Upon addition of SiO_2 colloids the effective solution concentration of the MV^{2+} quencher decreases due to adsorption. This results in an increase in the lifetime of the sensitizer triplet. From the dependence of the quenching rate on SiO_2 concentration one can construct an adsorption isotherm and thus the saturation level of the particles. The average number of negative charges on each SiO_2 colloidal particle was determined to be 32 (charge density = 0.09 C m^{-2} or 0.55 charges per nm^2). The value measured is approximately half that obtained by Calvin and co-workers.[9]

Willner and co-workers studied Rose Bengal–MV^{2+} complexes and their dissociation in aqueous SiO_2 colloids.[13] From the changes in the charge-transfer absorption band of the complex vs SiO_2 concentration they concluded that each particle can bear up to 22 $\pm$ 3 MV^{2+} molecules and thus neutralize 44 $\pm$ 6 charged sites. From their data, one can calculate a surface charge density of ~0.12 C m^{-2} or 1.5 charges nm^{-2}. The equilibrium constant for MV^{2+} adsorption on silica surface was found to be $K = (1.4 \pm 0.2) \times 10^5$ M^{-1}. More recently, Schnabel and co-workers studied adsorption of $Ru(bpy)_3^{2+}$ on Ludox 13.5 nm silica particles at pH 9.8. They conclude that the number of binding sites per particle is equal to 458, which translates to 0.8 charges per nm^2 on these larger particles.[14]

We report here on measurements of the number of adsorbed molecules per silica particle and the corresponding equilibrium constants for $Ru(bpy)_3^{2+}$ and MV^{2+} adsorption on Ludox silica

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particles of several sizes. We used the pulse radiolysis technique as an analytical tool to measure the bulk free adsorbate concentration by measuring the rate of hydrated electron decay in the presence and absence of the particles. In these measurements no centrifugation of colloidal particles in order to separate the free adsorbate from the molecules adsorbed onto the particles, is necessary. The effect of precipitation of the particles has plagued many efforts to determine adsorption parameters in aqueous suspensions.[15,16] It is also pertinent to note that the presently utilized method allows the measurement of adsorption parameters under the same conditions where radiolytic yields are to be measured.[8]
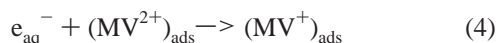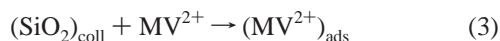
Experimental Section

Pulse radiolysis experiments were performed using 2 ns pulses of 8 MeV electrons from the Notre Dame Radiation Laboratory linear accelerator (TB-8/16−1S linac). Details of the linac, the spectrophotometric detection setup, and the computer-controlled data acquisition and detection systems are described elsewhere.[17] All measurements were performed at 18 °C degrees in a high purity silica cell of 1 cm optical path length. The concentration of radicals generated was approximately 2×10^{-6} M per pulse as determined by the thiocyanate dosimeter. All solutions were deaerated by bubbling N_2 for at least 30 min immediately prior to irradiation.

Tris(2,2′-bipyridyl)ruthenium(II) dichloride hexahydrate salt, methyl viologen dichloride hydrate salt, and NaOH (Aldrich) were of the highest purity commercially available and used as received. Three types of Ludox colloidal silica dispersions (Aldrich) were used: SM-30 (30 wt % SiO_2 in H_2O, pH = 10.2, specific surface area = 345 m^2 g^{-1} measured using the BET technique), HS-40 (40 wt % SiO_2 in H_2O, pH = 9.7, 220 m^2 g^{-1}), and TM-50 (50 wt % SiO_2 in H_2O, pH = 10.2, 140 m^2 g^{-1}). Soluble additives in the commercially obtained suspensions were removed by dialysis for several days prior to the radiolysis experiments against aqueous NaOH solution at pH = 10. These impurities shorten the lifetime of the hydrated electron by more than an order of magnitude, and therefore the dialysis was performed until its lifetime was restored to its value in the absence of the colloid.

Results and Discussion

To obtain adsorption isotherms we used pulse radiolysis as an analytical technique for measuring the adsorbate concentration in the bulk of the solution. A series of samples were prepared, each containing the same concentration of adsorbate (2.4×10^{-4} M) and various concentrations of colloidal silica. The decay of the hydrated electron, e_{aq}^-, was measured at 785 nm in N_2-saturated solutions, since there is a very little spectral overlap with other species involved at this wavelength. The relevant chemical reactions are listed below:

$$H_2O \rightsquigarrow e_{aq}^-, H, OH \tag{1}$$

$$e_{aq}^- + MV^{2+} \rightarrow MV^+ \tag{2}$$

$$(SiO_2)_{coll} + MV^{2+} \rightarrow (MV^{2+})_{ads} \tag{3}$$

$$e_{aq}^- + (MV^{2+})_{ads} \mathbin{-\!\!>} (MV^+)_{ads} \tag{4}$$

Among the radicals produced upon water radiolysis, only the hydrated electron is of relevance here since it is the only species followed in the present study. It is now well established that the silica particles do not react with the hydrated electron since
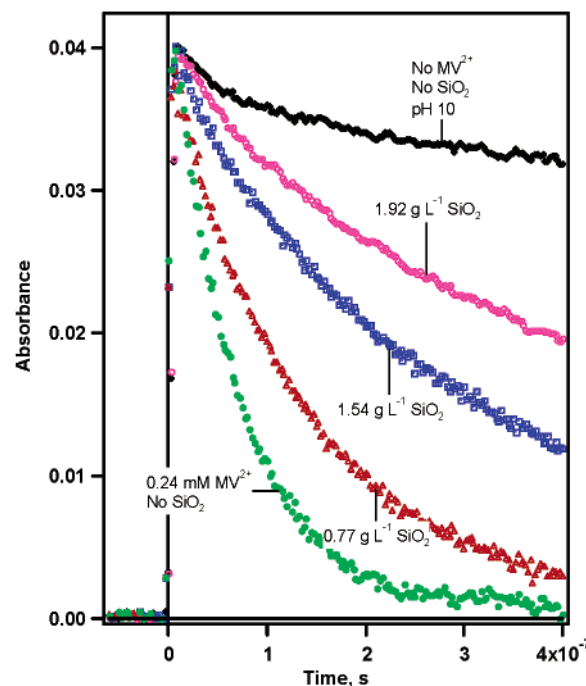
Figure 1. Histograms of the decay of e_{aq}^- measured at 785 nm at various colloidal silica (TM-50) concentrations in the presence of 2.4×10^{-4} M MV^{2+}. The slowest decay is in the absence of MV^{2+} and the fastest is in the absence of SiO_2.

the redox potential of the latter is approximately 2.6 eV below the conduction band of silica.[18] The rate constant for reaction 4 was measured earlier and it can be shown that the rate of the reaction of e_{aq}^- with adsorbed MV^{2+} molecules is negligible under all experimental conditions of the present study.[7] The smallest MV^{2+} concentration that can be measured with a satisfactory accuracy is 2×10^{-5} M if pseudo-first-order kinetics (eq 5) are to be employed in the data processing. At these concentrations the decay of e_{aq}^- was well described by pseudo-first-order kinetics for at least five half-lives. For lower MV^{2+} concentrations, various other reactions (such as radical−radical reactions) significantly compete for e_{aq}^-. For these low concentrations, the IBM Chemical Kinetic Simulator 1.01 computer software was used, as all the other reactions that take place must be taken into account.

Figure 1 shows the decay rate of e_{aq}^- as it reacts with MV^{2+}. As can be seen in this figure, the rate of decay slows down upon the addition of increasing amounts of SiO_2, as more MV^{2+} adsorbs on the particles. The measured decay rate, k_{obs}, is given by

$$k_{obs} = k_2[MV^{2+}]_{free} \tag{5}$$

where the rate constant for reaction 2, k_2, was determined in the absence of silica and the concentration $[MV^{2+}]_{free}$ refers to free methyl viologen in the solution. The value of k_2 was determined to be $(6.2 \pm 0.4) \times 10^{10}$ M^{-1} s^{-1}, at ionic strengths up to 0.5×10^{-3} M of $NaClO_4$, in close agreement with earlier determinations.[19] Then, the concentration of adsorbed viologen, $[MV^{2+}]_{ads}$, can be calculated as $[MV^{2+}]_{ads} = [MV^{2+}]_0 - [MV^{2+}]_{free}$, where $[MV^{2+}]_0$ is the total concentration of MV^{2+}. To simplify the experiments, $[MV^{2+}]_0$ was kept constant at 2.4×10^{-4} M. A single adsorption equilibrium constant, K, defined as

$$K = [MV^{2+}]_{ads}/\{[MV^{2+}]_{free}[sites]_{free}\} \tag{6}$$

Adsorption on Silica Nanoparticles

J. Phys. Chem. B, Vol. 108, No. 6, 2004 **1829**

TABLE 1: Adsorption Parameters Extracted from Adsorption Isotherms Presented for MV^{2+} and $Ru(bpy)_3^{2+}$

adsorbate/silica brand	particle radius[a] (nm)	surface area[b] ($m^2\ g^{-1}$)	equilibrium constant K (M^{-1})	[binding sites] $\times 10^{-6}$ (mol g^{-1})	no. of binding sites n (molecules/particle)	density of binding sites (molecules m^{-2})
MV^{2+}/SM-30	3.8 (3.5)	345	5.0×10^5	350	120	0.62
MV^{2+}/HS-40	5.9 (6.0)	220	4.3×10^5	230	300	0.64
MV^{2+}/TM-50	9.3 (11)	140	4.5×10^5	130	670	0.57
$Ru(bpy)_3^{2+}$/SM-30	3.8 (3.5)		1.3×10^5	245	85	0.43

[a] From BET measurements. In parentheses are radii from TEM as provided by the manufacturer. [b] From BET measurements.
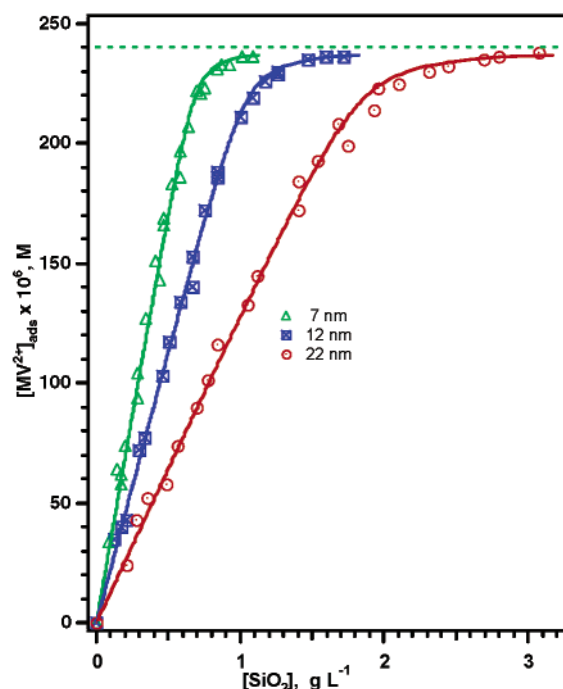
Figure 2. Adsorption isotherms for methyl viologen on colloidal silica particles of various sizes at pH = 10: TM-50, circles; HS-40, squares; SM-30 triangles. $[MV^{2+}]_0 = 2.4 \times 10^{-4}$ M. Silica concentrations are expressed in units of g L^{-1}.

Figure 3. Adsorption isotherms for methyl viologen on colloidal silica particles of various sizes at pH = 10: TM-50, squares; HS-40, circles; SM-30, triangles. $[MV^{2+}]_0 = 2.4 \times 10^{-4}$ M. Same data as for Figure 2 but silica concentrations are expressed in units of m^2.
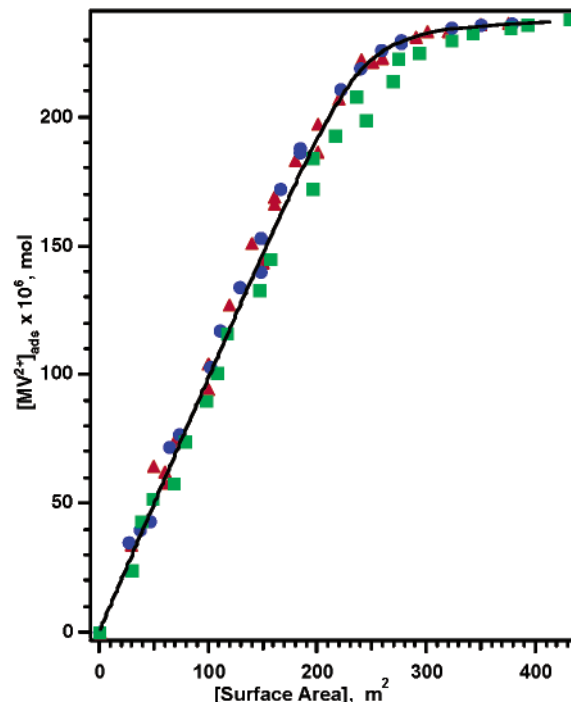
is assumed across this study. This assumption implies that the equilibrium constant is independent of occupancy of the adsorption sites.

The total concentration of adsorbing sites is equal to the product of the number of sites per particle, n, times the concentration of silica, $n[SiO_2]$. It is emphasized here that the number of sites is not an intrinsic property of the particles and depends on the adsorbate. For example, the number of sites in that context depends on the size of the adsorbed molecule and its orientation on the surface. Each site in this definition is occupied by a single adsorbate. With these assumptions the total number of sites per particle for a given adsorbate can be calculated from eq 7. The number of sites per particle, n, and the equilibrium constant, K, were determined from eq 7 using a nonlinear least-squares

$$n[SiO_2] = [MV^{2+}]_{ads} + \{[MV^{2+}]_{ads} /$$
$$([MV^{2+}]_0 - [MV^{2+}]_{ads})K\} \quad (7)$$

methodology. These are summarized in Table 1 for the adsorption of MV^{2+} (and $Ru(bpy)_3^{2+}$) on the various silica particles.

Comparing both the equilibrium constants and the density of binding sites for MV^{2+} adsorption, one notices that they are very similar for all thee Ludox particles. Thus, within experimental error ($\pm7\%$) the number of sites per particle and the

equilibrium constants are independent of particle size in this size regime. Figure 2 shows adsorption isotherms corresponding to adsorption of MV^{2+} on the various Ludox silica particles of the various sizes. The solid curves in this figure are the corresponding best fits to eq 7. The concentration of adsorbed MV^{2+} plotted as a function of the total surface area of the SiO_2 silica particles is shown in Figure 3. It is clear from this figure that the only parameter that determines the amount adsorbed is the surface area, independent of particle size. Since the same density of sites and adsorption constant were used to calculate the solid curve of Figure 3, these two parameters are also independent of the particle size. The average values used to plot the single solid curve in Figure 3 are $K = (4.7 \pm 0.3) \times 10^5$ M^{-1} and binding-site density of $(1.0 \pm 0.05) \times 10^{-6}$ mol m^{-2}.

Figure 4 compares adsorption isotherms corresponding to $Ru(bpy)_3^{2+}$ and MV^{2+} adsorptions on SM-30 colloidal silica suspensions. The best-fit values for the $Ru(bpy)_3^{2+}$ adsorption are $K = (1.3 \pm 0.1) \times 10^5$ M^{-1} and binding-site density of $(0.7 \pm 0.04) \times 10^{-6}$ mol m^{-2}. The smaller equilibrium constant is attributed to the different molecular sizes and the charge density distribution within the two molecules. For MV^{2+}, the positive charges are located on the nitrogen atoms and, therefore, can interact closely with negative charges on the silica surface. However, in $Ru(bpy)_3^{2+}$ the positive charge is mostly localized on the ruthenium ion at the center of the complex. The approach
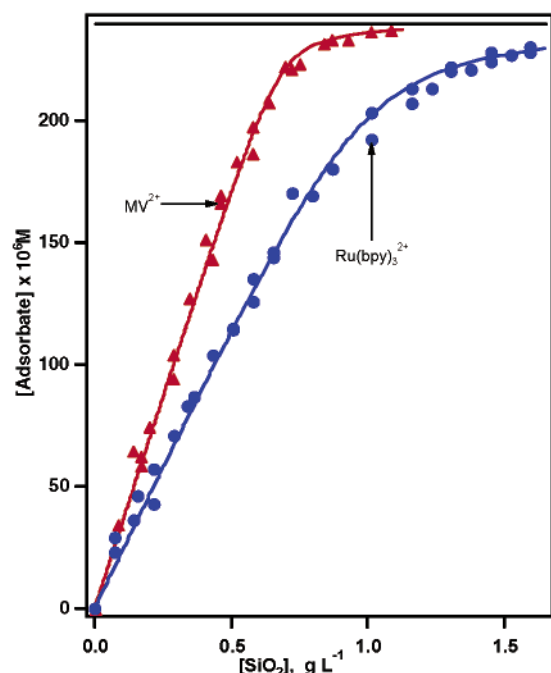
Figure 4. Adsorption isotherms for MV^{2+} and $Ru(bpy)_3^{2+}$ on SM-30 colloidal silica at pH = 10: MV^{2+}, triangles; $Ru(bpy)_3^{2+}$, circles. Total concentration of adsorbate is 2.4×10^{-4} M. Silica concentrations are expressed in units of g L^{-1}.

of the molecule to the surface, though, is hindered by the ligands. Thus, the electrostatic interaction at the adsorption site is significantly weaker.

As already mentioned above, the density of sites as defined in eq 7 may depend on the size of the adsorbed probe molecule. Apparently, the $Ru(bpy)_3^{2+}$ complex occupies a larger area when adsorbed on the silica particles than the MV^{2+} molecule. The results above indicate that the charge density on the particle is at least 1.2 charges nm^{-2} and it may be still larger. Estimates of the cross sections of MV^{2+} from molecular models indicate that it is ∼1.0 nm^2 provided the two rings are coplanar. Of course, there is no information on coplanarity in any of the present results and this calculation only indicates that the density of adsorbed molecules obtained above can easily be accommodated.

The observation of occupancy independent equilibrium constant in the various systems studied above is not a priori expected. The electrostatic attraction of the divalent molecule to the particles is expected to decrease as the loading increases (reaction 8).

$$(SiO_2)_{coll} \cdot (MV^{2+})_n + MV^{2+} \rightarrow (SiO_2)_{coll} \cdot (MV^{2+})_{n+1} \quad (8)$$
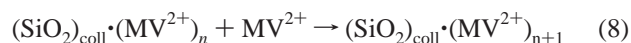
Yet, this effect seems to be too small to observe by the method used here. It should be recognized, though, that the results shown in Figures 2–4 are all at relatively high adsorbate loading. At low silica concentrations, along the linear portion of the curve in these figures, essentially all of the sites are occupied. Only at the curving end of the lines does the number of sites exceed the concentration of adsorbate. Even then, at the highest concentration of silica, 50% of the sites are occupied. Within these limits of 100% to 50% occupancy, the adsorption equilibrium constant is independent of loading within ±10%. It should also be noted that the adsorption−desorption equilibrium exists alongside the acid−base equilibria of the interfacial hydroxide groups. Therefore, some charge compensation is provided by the release of protons upon adsorption of MV^{2+}.

Conclusions

The equilibrium constant obtained for adsorption of MV^{2+} on the three different silica particles was found to be $K = (4.7 \pm 0.3) \times 10^5$ M^{-1}, independent of particle size (4 nm $\leq r \leq$ 10 nm) indicating that the binding sites and the interaction energy associated with them are identical. The density of binding sites was found to be $(1.0 \pm 0.05) \times 10^{-6}$ mol m^{-2} again independent of the particle size. On the other hand, for $Ru(bpy)_3^{2+}$ a significantly lower value of the equilibrium constant was obtained, $K = (1.3 \pm 0.1) \times 10^5$ M^{-1}, despite the fact that both the molecules have an identical charge. The binding-site density for the $Ru(bpy)_3^{2+}$ adsorption is 30% smaller than that for the MV^{2+}, 0.70×10^{-6} mol m^{-2}. The differences are attributed to different molecular sizes and the charge density distributions within them. The single equilibrium approximation was found to describe the adsorption reasonably well at surface loading of 100 to 50%.

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