

KINETICS OF RAPID SORPTION PROCESSES ON COLLOIDAL SURFACES

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Sorption processes on colloidal surfaces have traditionally been studied using macroscopic approaches. While data collected from these studies have been useful, no information is provided about the rates or mechanisms of the reactions. Much effort is currently underway to elucidate mechanisms for sorption of inorganic and organic species on colloidal surfaces using sophisticated microscopic and spectroscopic techniques. These approaches provide direct evidence for sorption mechanisms. However, unless one also monitors the reaction rates, no kinetic information is provided.

To definitively predict the mobility of metals, radionuclides, and organic contaminants in natural systems and their sorptive rates on sediments, metal oxides, clay minerals, humics, and soils, one must determine the kinetics of the reactions. In the past decade, a number of important and useful studies have appeared in the literature on various aspects of sorption kinetics on natural materials. The bulk of these studies have employed batch and flow techniques and reaction time scales of minutes and longer have been determined.

However, many sorption reactions on colloidal surfaces are quite rapid, occurring on millisecond and microsecond time scales. Examples of these include some metal and organic sorption/desorption reactions, ion exchange phenomena, redox transformations, reactions involving hydrolysis of minerals, and complexation reactions. Most traditional batch and flow methods cannot be used to measure such rapid reactions. Moreover, most of these methods measure a combination of transport and chemical kinetics. Consequently, the rate parameters one determines are apparent, and no chemical kinetics information is gathered.

To ascertain definitive rates and mechanisms of reactions on colloidal surfaces, one must measure the chemical kinetics, devoid of transport processes. Chemical relaxation methods afford a way to measure rapid sorption reactions and to determine chemical kinetics. These methods include pressure-jump, electric field pulse, concentration-jump, and temperature-jump. With these methods, the equilibrium of a reaction mixture is rapidly perturbed by some external factor e.g., pressure. Rate information can then be obtained by following the approach to a new equilibrium by measuring the relaxation time. The perturbation is small, and thus the final equilibrium state is close to the initial equilibrium state. Because of this, all rate expressions are reduced to first-order equations regardless of reaction order or molecularity. Thus, the rate expressions are linearized, simplifying determination of complex reaction mechanisms (Bernasconi, 1986; Sparks, 1989; Sparks and Zhang, 1991).

In this paper, theoretical and experimental aspects of pressure-jump and concentration-jump techniques will be discussed. Pressure-jump relaxation with conductivity detection was used to determine the rates of MoO_4 , SO_4 , SeO_4 , and SeO_3 adsorption/desorption at the goethite/water interface. Anion adsorption was best described by the modified triple layer model. Sulfate and SeO_4 adsorption occurred via outer-sphere complexation. The adsorption of MoO_4 and SeO_3 involved two steps: the first step resulted in the formation of an outer-sphere complex, and the second was a ligand exchange process which resulted in inner-sphere complexation. The second step was much slower than the first step. Intrinsic equilibrium constants obtained from the kinetic studies agreed with those measured from static studies.

An electron paramagnetic resonance stopped-flow (EPR-SF) kinetic method will also be discussed. With the EPR-SF technique, reactions involving an EPR active species can be directly monitored, *in situ*, on a millisecond time scale. This alleviates the necessity of using equilibrium based parameters needed in many relaxation techniques. We feel this technique has great utility for investigating the chemical kinetics of many environmentally important reactions in natural systems.

REFERENCES

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