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Fluorescence Thermometry of Porous Silica Heated by a Joule Discharge

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TEMPERATURE-JUMP RELAXATION KINETICS AT LIQUID/SOLID INTERFACES:
FLUORESCENCE THERMOMETRY OF POROUS SILICA HEATED BY A JOULE DISCHARGE

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Abstract

Temperature-jump relaxation techniques are adapted to measuring the kinetics of reversible reactions at liquid/solid interfaces. In the present work, we determine whether fast temperature changes can be created within a packed bed of silica gel using Joule discharge heating. Fast heating of the surface of porous silica depends on the solution within the pores carrying current through the particle, since heat flow from the surrounding solution into the interior of the silica particle would generally be slow. To characterize the rate of heating of the silica surface, fluorescence thermometry was employed to measure the temperature rise at a liquid/solid interface on a microsecond time-scale. 9,10 dichloroanthracene (9,10 DCA) was found to be a suitable probe molecule for fast fluorescence measurements of temperature changes at alkylated silica surfaces. For 10 μm silica particles, we observe an exponential relaxation of the temperature-dependent fluorescence intensity with a decay time that corresponds to the rate of energy deposition in the sample. These results indicate that ionic current flows through the silica, uniformly heating the surface area of smaller particle-size silica. Larger particle silica shows a slower thermal relaxation indicating non-conductive domains which are heated on a slower time-scale by thermal conduction.

BRIEF

Fluorescence from a 9,10 dichloroanthracene probe indicates that 10 μm C18-modified porous silica can be uniformly heated by a Joule discharge on time-scales of a few microseconds.

A number of phenomena important to analytical chemistry occur at interfaces between liquids and dielectric solids including adsorption, desorption, monolayer self-assembly, and reactions of immobilized reagents. Furthermore, a wide range of processes rely on selective interactions at these interfaces, such as surface protection and passivation, stabilizing composite materials, selective adsorption for larger scale separations, and surface modification for control of surface properties and heterogeneous reactions. While a great body of information exists for these phenomena and methods, most of our understanding of the dielectric solid-liquid interface has been inferred from measurements of surface concentrations, interfacial equilibria, adsorption isotherms, or other time-independent behavior of these systems. The subtlety of chemical interactions which play a role in these phenomena often cannot be sorted out with simple equilibrium measurements, where only the average, steady-state chemistry of the system is observed. Chemical kinetic measurements coupled with surface selective spectroscopies offer the opportunity for understanding reaction mechanisms responsible for the steady-state behavior and determining the dispersion of rates in cases where inhomogeneities lead to a distribution of transition state energies.

Among the measurement challenges which must be addressed to observe chemical reaction kinetics at dielectric solid/liquid interfaces is the need to rapidly change surface concentrations or activities, in order to observe the rates of surface reactions. This is particularly challenging for nonconductive solid surfaces where electrochemical perturbation to surface activities is not feasible, and where the rate of change of chemical composition at the interface is limited by molecular diffusion through a stagnant solvent layer adjacent to the solid surface. Several strategies for measuring reaction rates at

dielectric liquid-solid interfaces have been developed. For sufficiently slow kinetics, competitive reactions between a surface ligand and a mixture of reagents provide useful information, for example, about the relative rates of chlorosilane condensation reactions to silica [1]. Similarly, one can use flow methods to change the composition of the solution above a surface on a time-scale of seconds while spectroscopically monitoring a kinetic response. This approach has been used, for example, to measure rates of hydrolysis rates of chlorosilane reagents at silica surfaces [2,3]. On a nanosecond time-scale, pulsed laser generation of excited-states allows fluorescence decay rates to be measured, which can be used to determine the frequency of molecular encounters at the liquid/solid interface by observing excimer and exciplex formation [3-5] or fluorescence quenching of a surface-bound [6,7,8] or surface-sorbed probes [9].

These two methodologies leave a major gap in kinetic measurement time-scale undeveloped. For chemical reactions having rates which fall within the large range of intermediate time-scales from milliseconds to fractions of microseconds, flow methods are too slow and fluorescence decay kinetics are too fast. Relaxation kinetic methods [10,11] have the capability of spanning this range for chemical reactions which are reversible; with these methods, a chemical system is shifted from equilibrium by a rapid change in conditions (temperature, pressure, electric field), and the rate of relaxation of the reaction to the new equilibrium condition is measured.

Several successful examples of using relaxation methods for studying interfacial chemical kinetics have been published, all of which have employed a pressure-jump approach. The pressure-jump perturbation is particularly suitable for studying sorption/desorption kinetics of ionized species due to

the large change in molar volume which accompanies the process. Proton transfer rates on titanium and iron oxides [12,13], and proton transfer and adsorption rates for acetate on silica-alumina surfaces [14] have been determined by pressure-jump techniques using conductivity detection. More recently, the rates of ion-pair sorption to alkylated silica surfaces were measured [15,16] using fluorescence detection of the adsorbed probe. These latter studies showed that a dispersion in sorption energies can lead to distributions of desorption rates at solid interfaces which could be correlated with chromatographic band broadening.

The present work seeks to extend these studies by adapting temperature-jump relaxation techniques to measuring the kinetics of reversible reactions at liquid-solid interfaces. Temperature-jump techniques are the most general of the relaxation methods [11,17] since nearly every chemical equilibrium exhibits a finite enthalpy and therefore shows a variation with temperature. A temperature change is much more suitable than electric-field and pressure-jump for perturbing equilibria involving uncharged species. There are several methods of creating a fast temperature perturbation in a sample, including pulsed laser, microwave, and Joule discharge methods. We have chosen to evaluate Joule discharge heating since the instrumentation for this technique is relatively inexpensive and easy to construct. The temperature perturbation from a capacitor discharge can be relatively fast (on the order of 2-10 μ s or longer depending on the ionic strength of the solution being used), which could allow rate constants as fast as a 10^6 s^{-1} to be observed [11].

The focus of this study is to determine the feasibility of creating a temperature-jump perturbation within a packed bed of porous silica gel. Our interest in silica gel as a substrate for chemistry at liquid/solid interfaces

derives from its wide-spread use as a chromatographic support material and as a support for immobilized reagents. Porous silica is chemically and physically stable; it has a large specific surface area (100 to 500 m²/g) and is optically transparent from the ultraviolet through the near-IR, making it compatible with a variety of in situ optical spectroscopies. The feasibility of carrying out interfacial temperature-jump kinetic measurements in porous silica samples depends on whether the surface of the silica gel, more than 99% of which resides inside the porous particles, can be heated uniformly and quickly with a Joule discharge. Uniform heating depends on the solution within the pores of the silica carrying current through the particle, since heat flow from the surrounding conductive solution into the interior of the silica particle would be slow, requiring more than 10 μ s to uniformly heat the interior of a 10 μ m particle.

To test the feasibility of uniform fast Joule heating of silica, a temperature-jump cell was designed to contain a packed bed of silica gel. To characterize the rate of heating of the silica surface, fluorescence thermometry methods were adapted to measure the temperature rise of the liquid/solid interface on a microsecond time-scale. Several potential probe molecules were identified from the literature and evaluated to determine their suitability to the task by measuring the temperature dependence of fluorescence intensity, excited state lifetime, and affinity for C18-modified silica surfaces. Based on this evaluation, 9,10 dichloroanthracene (9,10 DCA) was found to be a suitable fluorescent probe molecule for fast fluorescence measurements of temperature changes at alkylated silica surfaces. The probe is used to determine the rate of heating of the surface of alkylated porous silica by a Joule discharge. For 10 μ m silica particles, we observe an exponential

relaxation of the temperature-dependent fluorescence intensity to its new value with a decay time that corresponds to the rate of energy deposition in the temperature-jump cell. These results indicate that ionic current flows through the silica pores, uniformly heating the surface area of smaller particle-size silica. Larger particle silica clearly shows a slower thermal relaxation component indicating non-conductive domains which are heated on a slower time-scale by thermal conduction from surrounding, electrically conductive domains.

EXPERIMENTAL SECTION

Materials. The microparticulate porous silica gels used in this study; Licrosorb Si-60 10 μm particle size and Licroprep Si-60 40-63 μm particle size. Licrosorb Si-60 and Licroprep Si-60 have mean pore diameters of 60 angstroms and a surface area of 550 square meters per gram (by N_2 BET). Dimethyloctadecylchlorosilane (ODS) and trimethylchlorosilane (TMCS) were purchased from Petrarch. Methanol, toluene, chloroform, tetrahydrofuran, and acetonitrile solvents were all spectral grade (OmniSolve).

The porous silica was derivatized by the following procedure. Three grams of the silica was placed in a dry reaction vessel consisting of a three neck flask, addition funnel, condenser and stopcock valve to allow evacuation and blanketing with dry nitrogen. The silica was evacuated to sub-millitorr pressures, heated to 110°C and kept under vacuum for 24h, cooled to room temperature (under constant vacuum) and purged with a positive flow of dry nitrogen to assure that adsorbed water was removed. Dry toluene (30 mL, stored over molecular sieves) and 3 mL triethylamine (Fisher scientific), serving as a catalyst, were added to the reaction vessel, taking care to avoid contact with the air. A five-fold molar equivalent excess of ODS (based on the silanol

density of the silica [18]) was dissolved in 10 mL of toluene and transferred to an addition funnel. This solution was added drop wise to the constantly stirred silica/toluene slurry. The addition funnel was removed and the solution heated to reflux for 24h. After the reaction cooled the resulting derivatized silica was washed with 6 x 150 mL of toluene, chloroform, tetrahydrofuran, acetonitrile and methanol. The derivatized silica was then air dried and placed in a clean reaction vessel, evacuated to sub-millitorr pressure, heated to 50°C and evacuated for 24h in preparation for endcapping. The procedure for endcapping is the same as above except TMCS is the derivatizing reagent and the reaction time was two hours. This final product was washed as above and again evacuated at 50°C to remove solvent. Elemental carbon and hydrogen analysis was performed by M-H-W Laboratories (P.O. Box 15149, Phoenix, AZ 85018). The silica was found to have a specific fraction of: 18.33% carbon and 3.87% hydrogen for the 10 μm particles and 22.86% carbon and 4.39% hydrogen for the 40-63 μm particles.

To characterize the Joule heating of these silicas, the temperature dependence of fluorescence of two probe molecules europium (III) thenoyltri-fluoroacetate, $\text{Eu}(\text{TFA})_3$ (Kodak), and 9,10 dichloroanthracene (Aldrich) were evaluated. Solutions of methanol/water with sodium chloride (Mallinckrodt) as the electrolyte were used in temperature dependent fluorescence and temperature-jump studies, and in chromatographic measurements.

Instrumentation. Fluorescence spectra of 9,10 DCA and $\text{Eu}(\text{TFA})_3$ were acquired using a Farrand Optical Model 801 scanning fluorometer; temperature control was provided by a Haake D3 constant temperature bath which circulated ethylene glycol to a jacketed cell holder. Temperature measurements were provided by a Fluka 52 K/J thermometer with the thermocouple between the cell

jacket and the sample cell. Fluorescence lifetimes were measured on two different pulsed laser, time-resolved fluorometers. The fast excited-state decay kinetics of 9,10 DCA were measured by using time-correlated single photon counting with a frequency-doubled, synchronously-pumped dye laser instrument, previously described [7,19]. The much slower fluorescence decay kinetics of $\text{Eu}(\text{TTA})_3$ were measured with a Nd:YAG laser-pumped dye laser and a 150 MHz bandwidth digital scope for data acquisition as previously described [20]. Chromatographic retention measurements were made using an HPLC system made up of a Beckman Model 210 injector, an Isco Model 2350 isocratic pump, a 25 cm, 10 μm ODS-II column from Whatman, and a Beckman Model 153 detector operated at 254 nm. Retention values of the probe molecules were determined relative to D_2O which has a negligible retention on ODS surfaces [21].

Temperature-jump measurements were performed using a Joule discharge apparatus, constructed locally, consisting of a Hipotronics R20B high voltage power supply, Maxwell 0.02 μF , 45 KV capacitor, EG&G TM-27 Thyatron driver, EG&G HY1102 grounded grid thyatron wired according to the circuit described in EG&G data sheet H5003G-3. Two temperature-jump sample cells were used; one cell was a stopped-flow temperature-jump cell from HiTech which was employed for free solution measurements. A second temperature-jump sample cell was designed and constructed in house to contain silica gel samples. The criteria for the design of this cell included small sample volume (38 μl), electrode gap (4.8 mm) and area (7.9 mm^2). A stainless steel frit, 3.2 mm diameter and 2 μm pore size from Mott Metallurgical (Farmington, CT), was fitted into the sample outlet of the cell to retain the silica gel packing. Details of the cell design are available upon request. Loading silica samples into the cell was accomplished by standard slurry packing techniques. Aqueous methanol solutions

containing the probe molecules and varying ionic strength were pumped through the cell at a rate of 0.2 mL/min using a Beckman 110A HPLC pump. Temperature-jump measurements were performed every 90 seconds, and averaged until a reasonable signal-to-noise ratio was achieved (usually 10 shots were averaged).

Radiation for fluorescence excitation was provided by a Coherent Innova 90 krypton ion laser producing 200 mW in two lines at 350.7 nm and 356.4 nm. In order to avoid heating or photobleaching the sample from constant illumination, a Uniblitz shutter unit was used to block the laser beam at all times except for several milliseconds before and during the temperature-jump measurements. The fluorescence from free solution samples was measured at a 90° from the incident laser radiation through a window in the HiTech cell. Fluorescence from silica samples was measured at a 180° from the incident laser radiation through a bifurcated fiber optic bundle constructed locally and fitted into the sample cell. The center fiber provided excitation and the surrounding 6 fibers provided collection of the fluorescence from the sample. Fluorescence was passed through a glass cutoff filter (Schott, 0-51) to remove any scattered laser radiation and detected using a Hamamatsu R928 photomultiplier tube; current from the detector was converted via a 1.0 kohm terminating resistor to a signal voltage, which was acquired and averaged using a Lecroy Model 9400 digital oscilloscope. The signal was transferred to a PC-AT for plotting and analysis.

RESULTS AND DISCUSSION

Characterization of Fluorescence Thermometry Probes. In order to determine whether porous silica gel heats uniformly in a Joule discharge, two fluorescent probes, europium (III) thenoyltrifluoroacetate ($\text{Eu}(\text{TTA})_3$) [22-23] and 9,10 dichloroanthracene (9,10 DCA) [24-25] were examined. The fluorescence quantum efficiencies of both of these molecules have been reported [22-25] to depend on temperature. Fluorescence from the europium complex has previously been used for thermometry applications in imaging [26]; its response time as a temperature probe has not been reported. The temperature dependence of the fluorescence intensity of each of these two probe molecules was measured between 24°C - 52°C, and the results are plotted in Figure 1. As seen from the results in the figure, the fluorescence intensity of both of these probes decreases linearly with increasing temperature. It is also apparent that the fluorescence of $\text{Eu}(\text{TTA})_3$ is considerably more sensitive to changes in temperature. The slopes of the two lines in Figure 1 are -0.60%/°C and -1.87%/°C, indicating a 3-fold higher temperature sensitivity for the europium probe.

The response of these two probes to a temperature-jump perturbation in free solution was also evaluated. The heating of the sample solution follows the exponential decay of the voltage from the capacitor discharge given by:

$$E(t) = E_0 \exp(-t/\tau_V) \quad (1)$$

where E_0 is the initial voltage and where $\tau_V (= RC)$ is the decay time of the voltage waveform which is equal to the product of the cell resistance and the capacitance of the high voltage capacitor, $C = 0.02 \mu\text{F}$. The power deposited into the sample is proportional to the square of the applied voltage: $P(t) = E^2/R$. On a short time-scale compared to thermal conduction of heat out of the discharge zone (seconds), the temperature of the sample rises with the

accumulated energy, $Q(t)$, equal to the integral of the deposited power:

$$\begin{aligned}\Delta T(t) &= Q(t)/\rho C_p V = (1/\rho C_p V) \int P(t) dt \\ &= (C E_0^2/2\rho C_p V) [1 - \exp(-2t/\tau_V)]\end{aligned}\quad (2)$$

where ρ , C_p , and V are the sample density, specific heat or heat capacity, and volume respectively. Note that the increase in the sample temperature rises exponentially at a rate, $2/\tau_V$, which is twice the rate of decay of the capacitor voltage (due to the power depending on the square of the voltage).

If a fluorescent probe in the sample responds linearly to changes in the sample temperature, one would expect the change in the fluorescence intensity to follow the exponential change in sample temperature according to:

$$I_f(t) = I_f(0) + \Delta I_f [1 - \exp(-t/\tau_{\Delta I_f})] \quad (3)$$

where $I_f(t)$ is the fluorescence intensity as a function of time, $I_f(0)$ is the initial fluorescence intensity (before the temperature-jump), ΔI_f is the total change in fluorescence intensity (proportional to the total change in sample temperature) and $\tau_{\Delta I_f}$ is the decay time of the fluorescence intensity change. According to Equation 2, the change in fluorescence should have a decay time, $\tau_{\Delta I_f} = \tau_V/2$ or half the decay time of the voltage discharge.

In order to test whether the two fluorescent molecules are well behaved thermometry probes on a microsecond time-scale, samples of the probes were prepared in solutions of differing ionic strength to vary the solution resistance which in turn varies the decay of the voltage discharge. The rate of energy deposited in the sample cell was determined by monitoring the voltage discharge, and the results were compared to the fluorescence response of the two probes in Table I. An example fluorescence transient is shown in Figure 2 for 10 μM 9,10 DCA in 60/40 methanol/water. Despite the limited signal-to-noise ratio of this data due to the small solubility of the probe in aqueous

solution, the single exponential time response of the probe is evident. Based on the temperature sensitivity of fluorescence of 9,10 DCA from Figure 1, the magnitude of the temperature change in Figure 2 can be estimated to be $\Delta T = 6.0 (\pm 0.5) ^\circ\text{K}$. This estimate compares reasonably with the prediction of Equation 2, $\Delta T = 7.2 ^\circ\text{K}$, obtained from known values of the capacitance, initial voltage, sample volume, and the specific heat and density of the mixed solvent [27]. The temperature rise predicted by Equation 2 has some uncertainty, arising from the unknown fraction of electrical energy lost to inefficiencies in electron transfer processes at the electrode/solution interface.

Based on the results in Table I, it is clear that the fluorescence of the 9,10 DCA probe accurately reflects the heating rate from the time-dependent change in the sample temperature. The decay times for the fluorescence intensity change agree within their uncertainties with the corresponding decay times for the voltage discharge. This behavior is quite different from that observed with the $\text{Eu}(\text{TTA})_3$ probe, where agreement is observed only at the longest discharge time but no agreement is apparent for the shorter discharge times. The apparently slow response of the $\text{Eu}(\text{TTA})_3$ probe, compared to the fast temperature response by 9,10 DCA, can be explained by the large difference in fluorescence lifetimes of these two probe molecules. The fluorescence lifetime of 9,10 DCA in 60/40 methanol/water solution was measured and found to be $5.9 (\pm 0.2) \text{ ns}$. A fluorescence lifetime would indicate that upon continuous illumination during a change in temperature, the excited-state kinetics can quickly reach a new steady-state condition, and the fluorescence yield responds to a change in temperature on a sub-microsecond time-scale. The weakly emitting f-f transitions of the $\text{Eu}(\text{TTA})_3$ complex, on the other hand, were found to produce a much longer fluorescence lifetime, varying from $89 \mu\text{s}$ to $73 \mu\text{s}$ in

40/60 methanol/water solution room temperature as the salt concentration is increased over the range listed in Table I. These results explain the sluggish response of the europium probe to a temperature perturbation since a temperature-dependent change in the excited-state kinetics cannot affect the steady-state emission yield faster than the excited-state population can evolve. The relaxation time to a fast temperature change is not expected to agree with the excited-state lifetime, since the rate of approach to steady-state includes both excitation and decay kinetics and is faster than either rate alone [11].

While the $\text{Eu}(\text{TTA})_3$ molecule is a more sensitive probe of temperature changes than 9,10 DCA, use of the europium probe is limited to time-scales longer than 100 μs . A final issue concerning the use of either of these probes for measuring interfacial temperature changes in porous solids is the surface concentration of the probe compared to its concentration in free solution. Since Joule heating of silica requires current flow through a conductive solution, aqueous solutions were chosen for these studies to allow solubility of dissolved electrolyte. This choice required the use of reversed-phase (C18) chromatographic surfaces to retain probe molecules by adsorption (since aqueous solutions would strongly displace adsorbates from bare silica surfaces). The affinities of the $\text{Eu}(\text{TTA})_3$ and 9,10 DCA probes for C18-modified porous silica was tested chromatographically for several methanol/water solutions, and the results are listed in Table II. The results listed are capacity factors, k' , defined as the moles of retained solute ratioed to the moles in solution and measured by a ratio of retention times:

$$k' = V_S C_S / V_M C_M = (t_r - t_m) / t_m \quad (4)$$

where t_r is the retention time of the probe t_m is the retention time of an unretained species (D_2O), $V_S C_S$ and $V_M C_M$ are the volumes and analyte concentra-

tions for the stationary phase and mobile phase, respectively. Thus, $1/(k'+1)$ is the fraction of probe molecules in the solution, the largest volume of which is between the silica particles. From the results in Table II, it is clear that only the hydrophobic probe, 9,10 DCA, in solutions containing at least 20% water would be free of a solution phase interference problem. At 60/40 methanol/water conditions, more than 40% of the $\text{Eu}(\text{TTA})_3$ probe molecules would reside in solution, while for 9,10 DCA, the solution interference would be less than 0.04%.

Joule Heating of the Porous Silica/Solution Interface. The question of whether the interfacial temperature-jump kinetic measurements can be successfully carried out with silica gel samples depends on whether surface of the silica can be quickly and uniformly heated with a Joule discharge. Since >99% of the surface area of silica gel resides inside the porous particles, uniform heating requires that the solution within the pores of the gel carry current through the particle. Heating by thermal conduction from the surrounding liquid solution into the interior of the silica particle would generally be slow unless very small silica particles were used.

Deriving an accurate model for heat-flow from solution into irregular silica particles, to predict the rate of this process, is difficult due to the irregular shape and non-uniform size of the particles. A rough estimate of the time-scale for heating by thermal conductivity from solution (assuming the silica has no bulk electrical conductivity) was obtained, however, from a published solution to differential equation for heat conduction into a sphere from a constant temperature change at the surface, where the time dependence of the change in the volume-weighted average temperature of the sphere is given by [28]:

$$\Delta T_{avg} = \Delta T_0 - (6 \Delta T_0 / \pi^2) \sum_{n=1}^{\infty} (1/n^2) \exp(-n^2 D \pi^2 t / r^2) \quad (5)$$

where ΔT_0 is the temperature change at the surface of the sphere of radius, r , and where $D = k/\rho C_p$ is the thermal diffusivity which is equal to the thermal conductivity divided by density and heat capacity. Using a volume-weighted average value for the thermal conductivity, density, and heat capacity of amorphous silica and mixed methanol/water solvent to estimate D , Equation 5 predicts that the time required to raise the average temperature of a 10 μm diameter spherical silica particle by thermal conductivity to 90% of a steady-state value would be ca. 12 μs , while the time required to reach this same condition for 50 μm silica particles would be ca. 290 μs . These time estimates should be considered lower bounds, since the boundary conditions for Equation 5 specify a constant temperature at the surface of the spherical particle. The actual rates of the temperature rise would generally be slower due to the decrease in the surface temperature from heat flow into the particle and the finite thermal conductivity of the solvent.

To test whether the interior surface of silica gel can be heated on a time-scale sufficiently fast to study interfacial relaxation kinetics by passing a Joule discharge through a packed bed of silica gel, 9,10 DCA at 10 μM concentration in 60/40 methanol/water was equilibrated with the surface of 10 μm , C18 silica gel in a series of solutions containing different concentrations of NaCl electrolyte. From the chromatographic results presented in Table II and discussed above, the 9,10 DCA probe is strongly retained on C18 silica under these conditions so that the free-solution contribution to the observed fluorescence signal is negligible. Example temperature-jump response of the adsorbed probe in the porous silica is shown in Figures 3 and 4, and the

results are listed in Table III for different concentrations of electrolyte. One notices that the temperature changes in the silica samples are larger than for free solution (compare ΔT in Figure 2); this is not surprising since the heat capacity per unit volume of amorphous silica is 2-times greater [27] than the heat capacity of the methanol/water solution.

As seen in Figures 3 and 4, the temperature change of the C18 silica surface, reflected in the sorbed probe fluorescence, is a single exponential response having a relaxation time which agrees within the experimental error with the decay time of the voltage discharge as listed in Table III. For the 10 μm diameter silica, there is no detectable delay in the surface heating at times as short as fractions of microseconds. Based on Equation 5, heat flow by thermal conduction from solution would have a time constant (time required to reach $1/e$ of the steady-state response) of $\geq 4 \mu\text{s}$. Significant heating of the silica by this process would have increased the relaxation time for the 0.8 M electrolyte results by several microseconds relative to the decay time of the discharge. The lack of any detectable delay in the heating of the silica surface, therefore, indicates that conductive solution in the 10 μm silica pores carries significant discharge current through the particle.

While the electrolyte solution within 10 μm silica appears to produce bulk conductivity through the particle, we were interested to learn whether this property would extend to larger particle silica. A sample of same 60 Å pore-size silica gel having a 5-times larger particle size (40-63 μm) was surface-modified with C18 chains as above, and temperature-jumps by Joule discharge were performed using the 9,10 DCA fluorescence probe. A typical fluorescence response for 9,10 DCA is shown in Figure 5. The fluorescence response is clearly not a single exponential. Furthermore, the decay time of the energy

from the voltage discharge, $\tau_V/2 = 35 \mu\text{S}$, is slightly faster than the temperature rise of the sample. The fluorescence probe response to the temperature change of the sample was fit successfully to a bi-exponential model, where $\tau_1 = 56 (\pm 4) \mu\text{S}$ and $\tau_2 = 422 (\pm 66) \mu\text{S}$ accounted for 75% and 25% of the amplitude of the temperature change, respectively. These results clearly show that the larger particle silica has domains which lack bulk conductivity and which are raised in temperature only by the slow flow of heat from other regions. The slower relaxation time agrees in order-of-magnitude with the lower limit for the time of heat flow into $50 \mu\text{m}$ diameter spheres predicted by Equation 5. Even in the presence of insulating regions within the larger particle silica (closed pores), domains near the surface of the particle were expected to remain conductive. The faster responding component to the relaxation indicates heating at a rate which is slightly slower than the decay of the voltage discharge. This behavior could be due to an outside conductive layer of the particle acting as a heat source for the interior during the discharge, which increases its relaxation time. Alternatively, charging the capacitance of the non-conductive domains in the silica could counter the applied field and reduce the current flow with time. Regardless of the cause, the bi-exponential equation used to fit the data of Figure 5 should not be interpreted too closely, since it provides only a description of the data and is not based on the heat flow physics.

The pore conductivity and heat flow in larger particle silica gel remains an interesting problem and is the subject of an on-going investigation [29]. The Joule discharge heating provides an unique tool for examining the connectivity and pore structure of silica gels, and deserves further work. More generally, the observation of prompt Joule heating of smaller particle-size

silica indicates that temperature-jump relaxation measurements should be a viable tool for following the kinetics of fast reversible reactions at the silica/solution interface.

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Table I. Free Solution Temperature-Jump Results

[NaCl] M	$\tau/2$ voltage (μS) ^a	$\tau \Delta I_f$ (μS) ^b
9,10 DCA in 60/40 Methanol/Water		
0.1	12.7 ($\pm$ 0.1)	14 ($\pm$ 2)
0.2	7.0 ($\pm$ 0.1)	7 ($\pm$ 1)
0.6	2.9 ($\pm$ 0.1)	4 ($\pm$ 1)
Eu(TTA) ₃ in 40/60 Methanol/Water		
0.01	138 ($\pm$ 4)	137 ($\pm$ 3)
0.05	25.3 ($\pm$ 0.5)	68 ($\pm$ 2)
0.1	12.7 ($\pm$ 0.4)	54 ($\pm$ 1)
0.2	7.0 ($\pm$ 0.2)	42 ($\pm$ 1)
0.4	4.1 ($\pm$ 0.1)	38 ($\pm$ 1)

^a Half the decay time of the voltage discharge.

^b Decay time of the fluorescence intensity change determined by least squares fitting of fluorescence transients.

Table II. Retention^a of Fluorescence Thermometry Probes
on C18-modified Porous Silica.

[MeOH/H ₂ O] ^b	Eu(TTA) ₃	9,10 DCA
100/0	0.13	2.94
80/20	0.42	39.2
60/40	1.32	>2000

^a Capacity factors, k' , relative to D₂O are tabulated.

^b Solvent composition in volume %.

Table III. Packed Bed Temperature-Jump Results^a

[NaCl] M	$\tau/2$ voltage (μs) ^b	$\tau \Delta I_f$ (μs) ^c
0.1	27.5 (± 0.2)	25 (± 2)
0.2	16.3 (± 0.2)	15 (± 1)
0.6	7.5 (± 0.2)	6.8 (± 0.6)
0.8	5.9 (± 0.1)	5.9 (± 0.4)

^a Sample is 10 μm C18 modified silica, and the fluorescence probe is 9,10 DCA.

^b Half the decay time of the voltage discharge.

^c Decay time of the fluorescence intensity change determined by least squares fitting of fluorescence transients.

FIGURE CAPTIONS

1. Temperature dependence of the fluorescence intensity of 9,10 DCA and $\text{Eu}(\text{TTA})_3$ in ethanol. Slopes of the two lines are $0.60\%/^{\circ}\text{C}$ and $1.87\%/^{\circ}\text{C}$, respectively.
2. Fluorescence-detected temperature-jump in free solution. The fluorescent probe is 9,10 DCA, $10\mu\text{M}$ in 60/40 methanol/water with 0.1 M NaCl electrolyte. Increasing intensity is downward. A scale marker for the temperature change is shown, based on the temperature sensitivity of the probe, and a least squares best fit to Equation 3 is plotted.
3. Fluorescence-detected temperature-jump in a packed bed of C18-modified, $10\mu\text{m}$ silica gel. The fluorescent probe is 9,10 DCA, $10\mu\text{M}$ in a solvent of 60/40 methanol/water (V/V) with 0.1 M NaCl added as supporting electrolyte. A scale marker for the temperature change is shown, and a least squares best fit to Equation 3 is plotted for $\tau = 25\mu\text{s}$.
4. Fluorescence-detected temperature-jump in a packed bed of C18-modified $10\mu\text{m}$ silica gel. The fluorescent probe is 9,10 DCA, $10\mu\text{M}$ in a solvent of 60/40 methanol/water (V/V) with 0.8 M NaCl added as supporting electrolyte. A least squares best fit to Equation 3 is plotted for $\tau = 5.9\mu\text{s}$.
5. Fluorescence-detected temperature-jump in a packed bed of C18-modified 40-63 μm silica gel. The fluorescent probe is 9,10 DCA, $10\mu\text{M}$ in a solvent of 60/40 methanol/water (V/V) with 0.2 M NaCl added as supporting electrolyte. A least squares best fit to a two-exponential relaxation is plotted for $\tau_1 = 56\mu\text{s}$ and $\tau_2 = 422\mu\text{s}$.

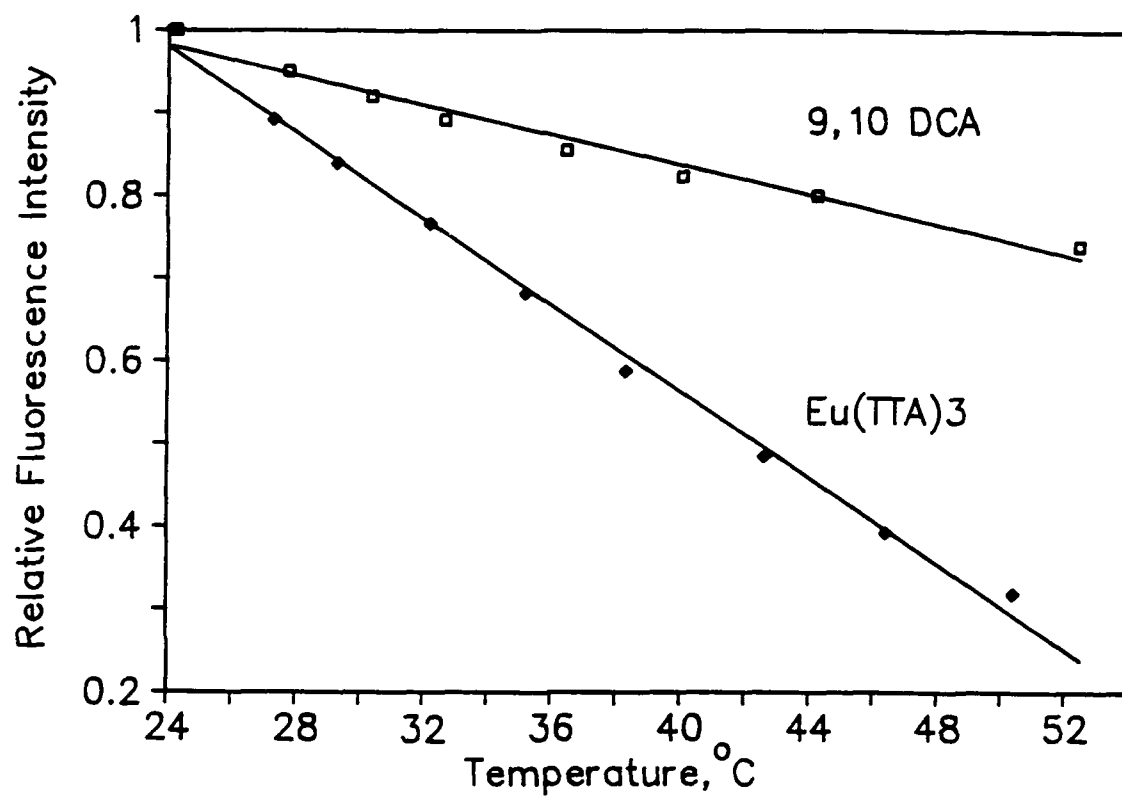


Figure 1

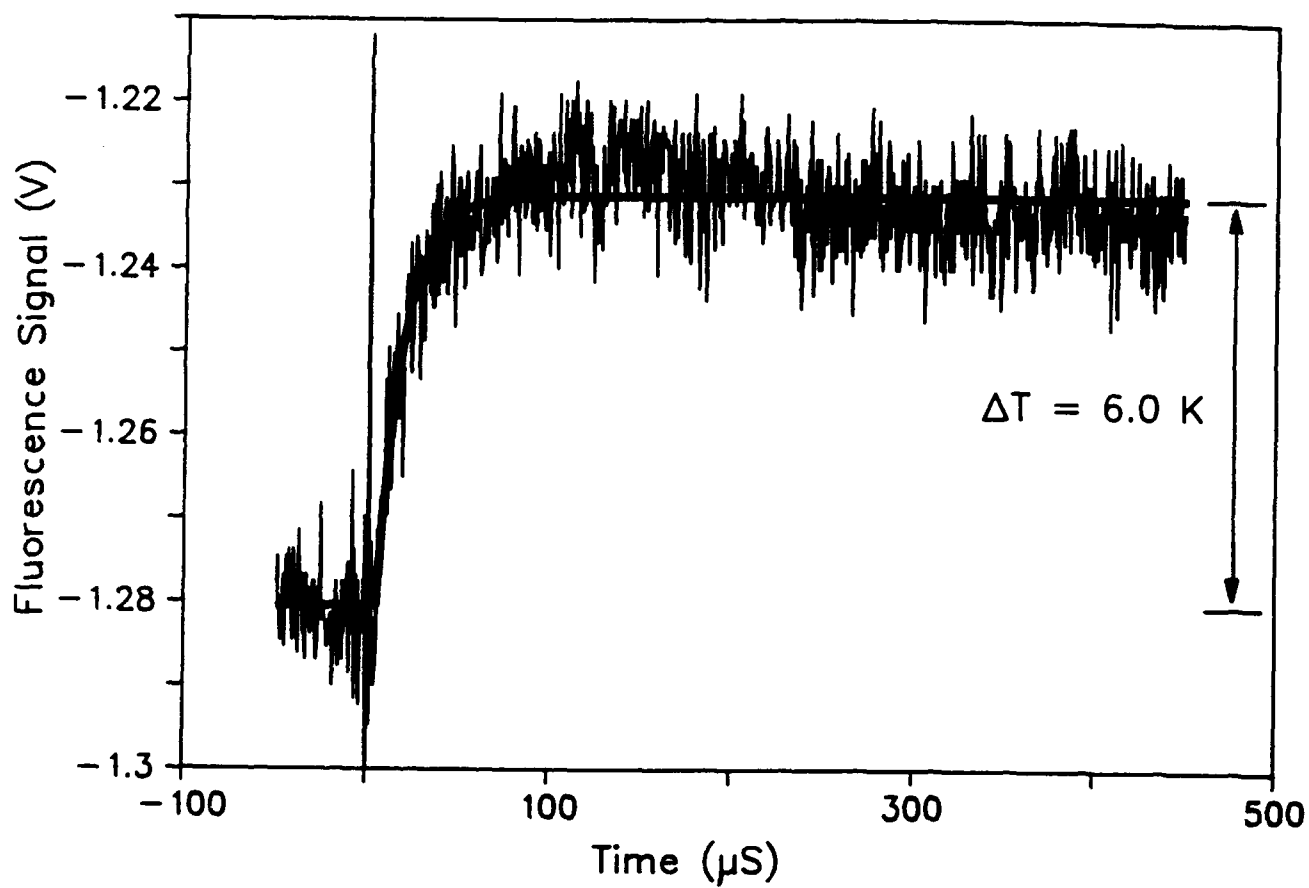


Figure 2

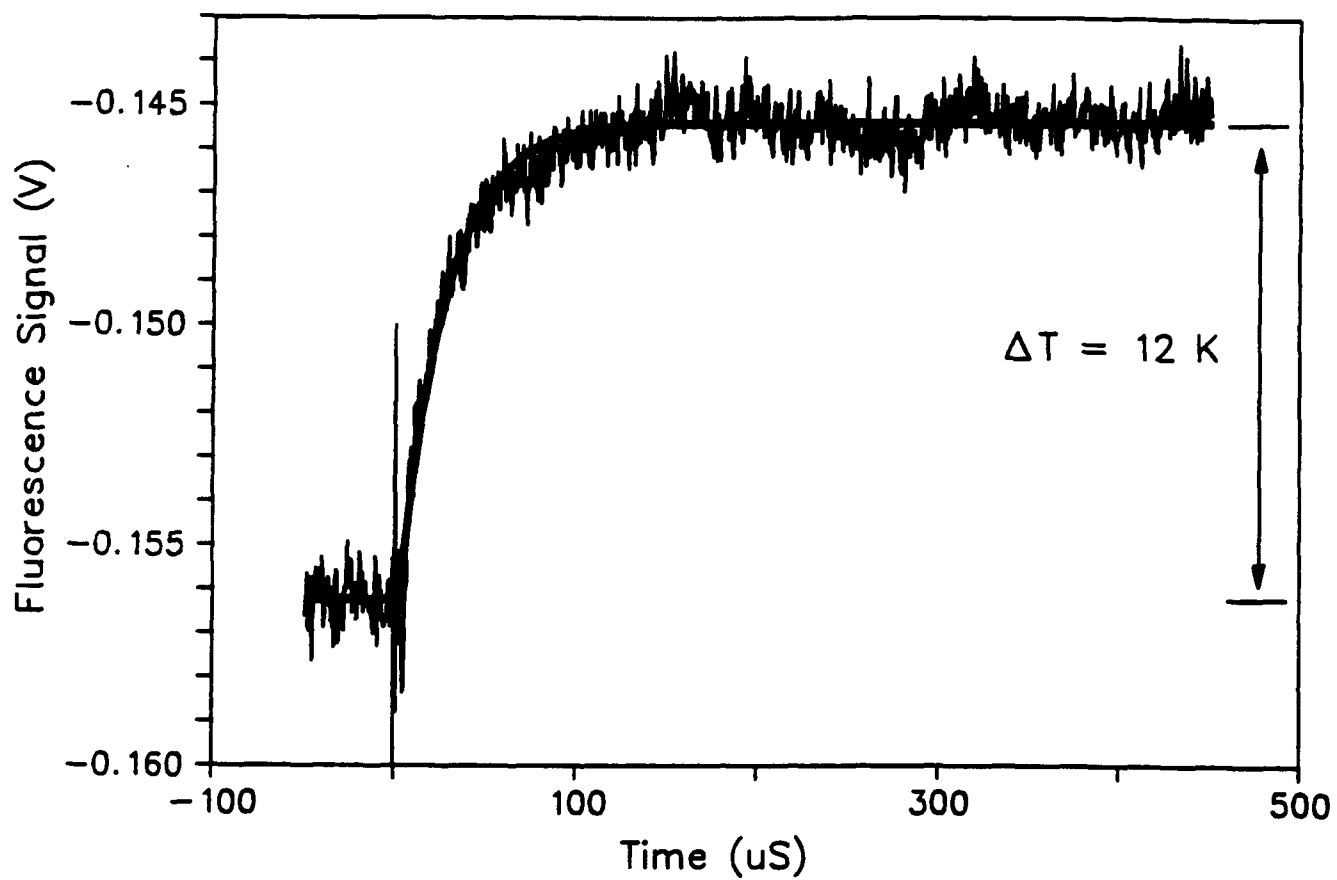


Figure 3

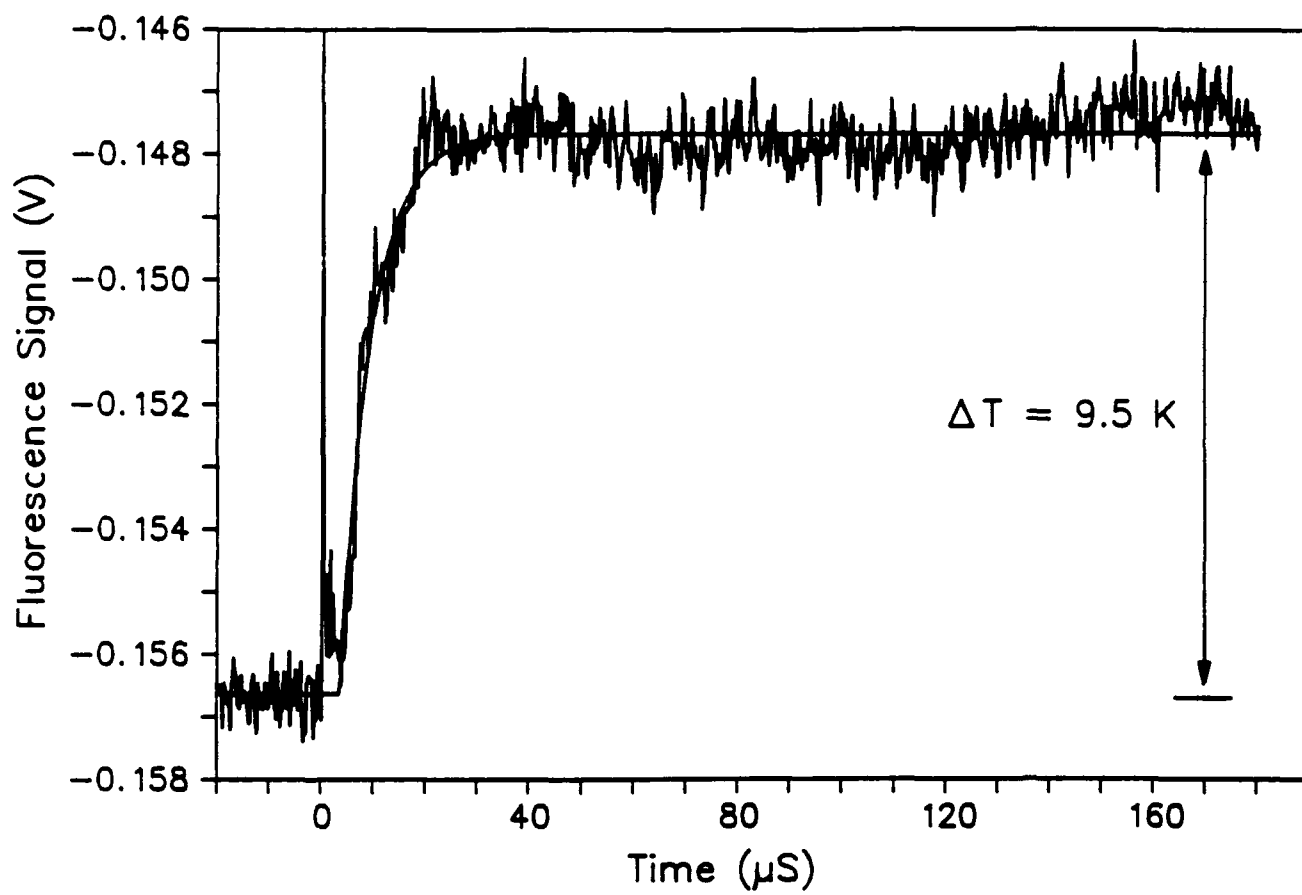


Figure 4

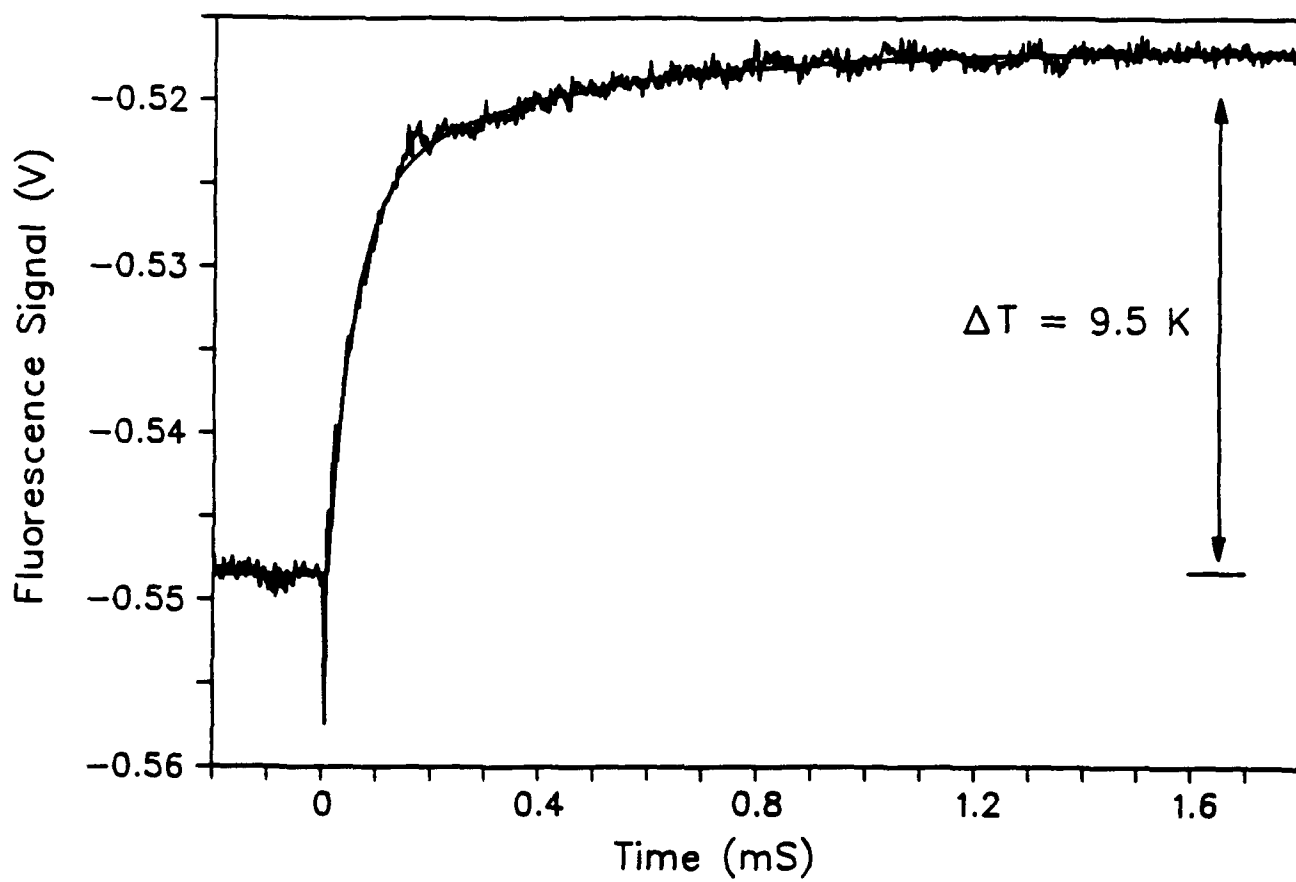


Figure 5