J. Am. Chem. Soc. **1987**, *109*, 1913-1916

Rotational Brownian Movement of Tungstic Acid Colloids As Studied by the Spectrophotometric and Conductance Stopped-Flow Techniques

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Received April 8, 1986

Abstract: Rotational-relaxation time and diffusion coefficient (D_r) of ellipsoidal colloids of tungstic acid in aqueous suspension are determined conveniently and precisely by the spectrophotometric and conductance stopped-flow techniques. The D_r values observed agree excellently with those calculated by Perrin's equation, especially for large colloids (major semiaxis, c, is between 2.5 and 3.0 μm). For the smaller colloids (c = 0.5–2.0 μm), the observed D_r values are smaller than the theoretical ones, and the deviation increases as the size decreases. This is ascribed to the significant contribution of the Debye–Hückel double-layer thickness (Debye screening length) in the absence of foreign salt.

The rotational diffusion coefficient (D_r) is a fundamental property of spherical and anisotropic colloids in suspension and also of flexible bio-polyelectrolytes, such as DNA. However, the experimental method for its determination is not always easy. Flow birefringence, non-Newtonian flow, electric birefringence, fluorescence depolarization, and dielectric dispersion are typical methods that have been studied so far.[1-4]

In this paper we propose a stopped-flow (SF) technique as a new and convenient method for determining the rotational relaxation times of anisotropic colloid particles such as ellipsoidal colloids of tungstic acid. The spectrophotometric stopped-flow (SP-SF) instrument can analyze fast reactions in the reaction rate range of 1 ms to several seconds.[5,6] In this instrument two kinds of solutions are mixed in a mixer cell and then the reaction solution is allowed to flow into an observation cell, a narrow tube usually 2 mm in diameter, at a significantly strong shear rate. The absorption change is recorded as a function of time just after the flow is stopped.

The asymmetric colloidal molecules should be oriented along the flow direction during the continuous flow due to the shearing forces arising from the velocity gradient. When the solution flow is stopped, the colloidal molecules revert to rotate freely in a Brownian random distribution. Translational diffusion is not very significant in the SF method, since the flow of the solvent molecules stops completely when the observation starts. For large ellipsoidal colloids, the multiple-scattering of light changes significantly with the orientation. Thus, absorbance would relax toward an equilibrium point after the stopped-flow. The solution conductance is also expected to change with time in the conductance stopped-flow (CSF) cell, because electrical anisotropy is also a significant factor in oriented liquid.[7-14] We have intensively studied many chemical and physical reactions by the CSF method hitherto. The reaction systems were micellar equilibria of ionic surfactants,[15] macroion-neutral polymer association,[16] macroion complexations with metal ions,[17] polyelectrolyte complexation between macrocations and macroanions,[18] enzymatic reactions,[19] and others.[20-23] It should be noted here that the mixing process is not needed in order to get rotational relaxation time. However, it is a convenient way of getting data for various experimental conditions of solute concentrations and ionic strength.

Experimental Section

Materials. Monodispersed ellipsoidal colloids of tungstic acid were prepared and purified by the method of Furusawa and Hachisu.[24] Sodium tungstate (Na_2WO_4) was purchased from Nakarai Chemicals Co., Kyoto (specially prepared reagent grade for biochemical studies). HCl (25 mL, 1 N) and 50 mL of 7 wt % Na_2WO_4 were refrigerated separately for more than 12 h before mixing. Then the two solutions were mixed, and the mixture was again refrigerated for 15 h. A slightly yellowish gel of tungstic acid colloids was obtained. After repeated centrifugation and dispersion in water (about five times), the suspension (1.5 L) was incubated in a thermostated bath (5–22 °C) for more than 24 h. Then the monodispersed crystalloids appeared. The colloids were further purified by repeated decantation. The conductance of the dispersed solution thus obtained was ca. $1 \times 10^{-5}\ \Omega^{-1}$. Lengths of the major axis ($2c$) and the middle one ($2b$) were determined by a reversed-type metallurgical microscope, Carl-Zeiss Axiomat IAC. A typical photograph of the colloids is shown in Figure 1. The cell used was the same as that described previously.[25] The length of the minor axis ($2a$) was not determined experimentally in this work but was estimated from data of a previous work on electrophoresis properties of the same colloids[24] and at the same solution temperature, since essentially the same method of preparation of the colloids was used. The present colloid is monodispersed and ellipsoidal, and $2a$ is very short (between 100 and 900 Å) compared with $2b$ and $2c$ (1.4–6 μm).[26,27] Figure 2 shows the relationship between $2b$ and $2c$ values of the crystalloids prepared in this work. The standard deviation of the $2b$ and $2c$ values was within 6%. The relation of $b = 0.43c$ held. Suda and Imai[28] reported a relation of $b = 0.30c$ for the same colloids, though their photograph showed a thin rectangle instead of an ellipsoid. Furusawa and Hachisu[26] reported a transformation of a colloid shape from ellipsoidal to rectangular with the lapse of time. The water used for the preparation of sample solutions was obtained by a Milli-Q water system (Type I, Millipore, Ltd., Bedford, MA).

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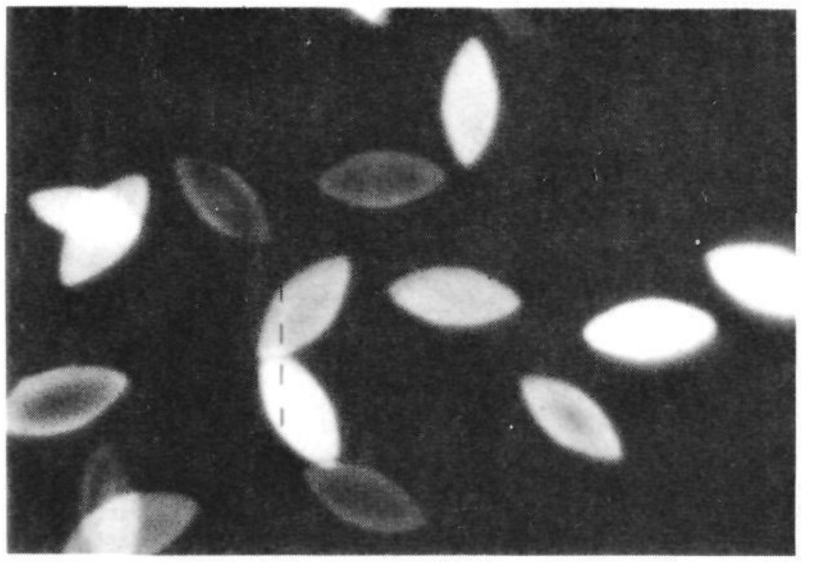

Figure 1. Microscope photograph of tungstic acid colloids in aqueous suspension. The distance between the two broken lines in 1 μm.

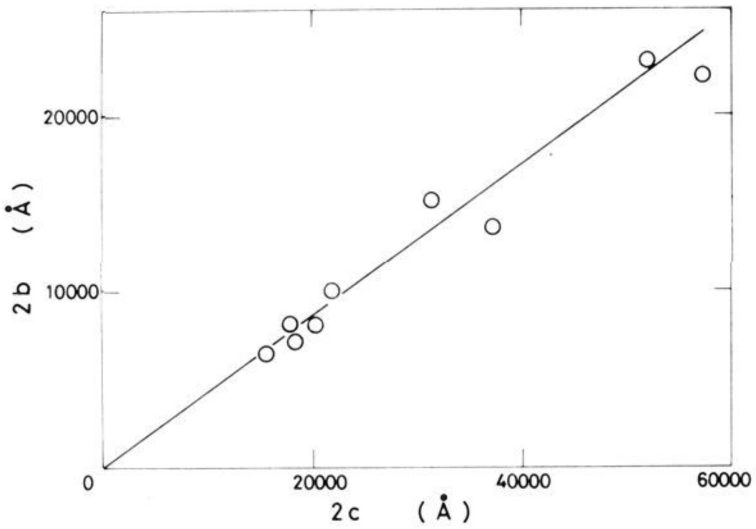

Figure 2. Relationship between the major axis (*c*) and middle axis (*b*) of tungstic acid colloids.

Electric Conductance, SP–SF, and CSF Measurements. Electric conductance was measured on a Wayne-Kerr autobalance precision bridge (Model B331, mark II) with a conductivity cell (Model 3452, Horiba, Kyoto, cell constant = 1.009). A stopped-flow spectrophotometer (RA-1100, Union Engineering, Hirakata, Japan) was used. The wavelength was 600 nm in most cases. The narrow light beam projected from the tungsten lamp source through two slits perpendicularly hits the observation cell, a quartz capillary (2 mm in inner-diameter and 10 mm in length). The light goes through a monochrometer and then a photomultiplier. The details of the CSF apparatus have been described in a previous paper.[15,23] The sample solution from the mixer, which was made of Teflon and a four-jet type, flowed through platinum plates. The platinum plate electrodes (2 mm × 10 mm) were fixed on opposite walls (2 mm apart) inside the observation cell made of epoxy resins. For each run, about 0.2 cm^3 of solution was required. A value of 1.30 cm^{-1} was obtained for the cell constant. An ac current of 50 kHz was given to the Wien bridge. The applied voltage across the cell was kept at 2 V (root mean square). The time change of the deviation of the solution conductance from its equilibrium value was amplified in two steps and monitored by a memoriscope and/or digital memory and an X–Y recorder after rectification. The dead time for both SP–SF and CSF instruments was 1 ms.

Rapid-Scanning Spectrum Measurements. Time change of the extinction spectra of tungstic acid colloid was recorded on a Multi-Channel-Photo-Detector (MCPD-110B, Union Engineering, Hirakata, Japan) connected to a stopped-flow mixer (type RA-401, Union Engineering). The instrument was operated with a microcomputer (MC800, Union Engineering). The light intensities at different wavelengths, interval of 0.1 and 150 nm in the whole range, were accumulated simultaneously during the "sampling time" preset (longer than 25 ms) and recorded. After the "interval time" preset (longer than 100 ms), the accumulation started over again, and the measurements were repeated a hundred times.

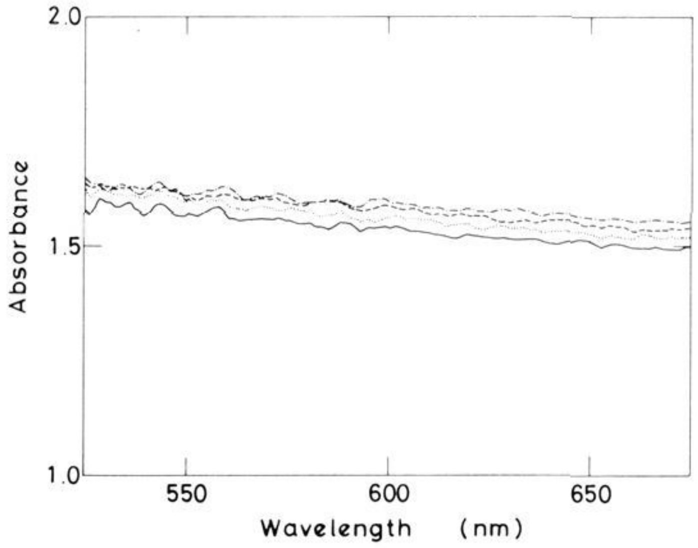

Figure 3. Transmitted light spectra of tungstic acid colloid. 0.32 wt %, $2a$ = 900 Å, $2b$ = 22 200 Å, $2c$ = 57 300 Å, (—) 0 s after flow stop, (···) 0.4 s, (- - -) 2.9 s, (-·-) 7.9. Sampling time = 25 ms, interval = 100 ms.

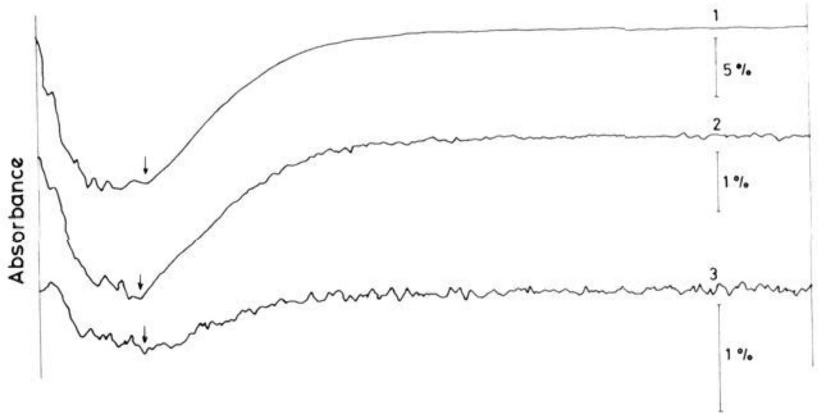

Figure 4. Typical traces of relaxation of SP–SF measurements of tungstic acid colloid. $2a$ = 100 Å, $2b$ = 6400 Å, $2c$ = 15 600 Å, Curve 1: 0.04 wt %, horizontal full scale = 2 s. Curve 2: 0.008, 2. Curve 3: 0.004, 2. Arrows show the instant of stopping the flow.

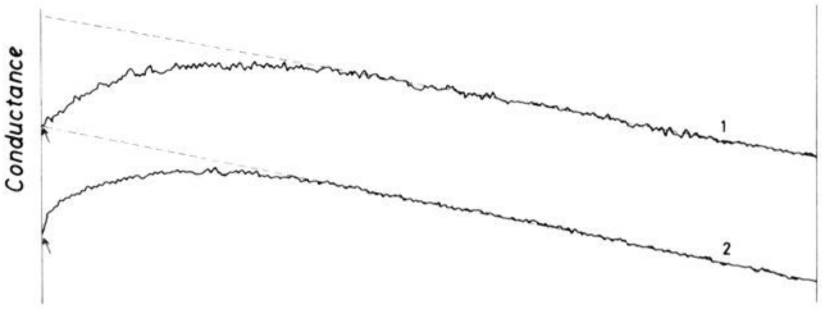

Figure 5. Typical traces of relaxation of CSF measurements of tungstic acid colloid. $2a$ = 700 Å, $2b$ = 23 000 Å, $2c$ = 52 000 Å. Curve 1: 0.082 wt %, horizontal full scale = 10 s. Curve 2: 0.062, 10. Arrows show the instant of stopping the flow.

Results and Discussion

Rapid scanning absorption spectra are shown in Figure 3. The ellipsoidal colloids used here were rather large, $2a$ = 900 Å, $2b$ = 22 200 Å, and $2c$ = 57 300 Å. Clearly, the strength of the transmitted light is high when the suspension flows through the observation cell. After the solution flow was stopped, the absorbance began to increase because the multiple-scattering of light increases when the rotational motion changes to a random orientation. The total change in the absorption is estimated to be roughly 5% in Figure 3, and quite enough to get reliable relaxation curves by the SP–SF measurements. Typical curves of the relaxation are shown in Figure 4. In these experiments the same solution was poured into two vessels and then mixed. It is clear that the absorption decreases abruptly with mixing and begins to increase again with time. From the first-order plot, the rotational relaxation time (τ) was obtained. The relaxation curves of the anisotropy in conductance were also obtained by the CSF measurements. Typical examples of the relaxations are shown in Figure 5. In this figure the same solution was also mixed. The linear decrease of the conductance in the figure indicates the existence of a very slow, additional relaxation step. The assignment is, however, not clear yet. The SP–SF and CSF methods gave the same values of relaxation times within experimental error.

The concentration dependence of relaxation time (τ) from the SP–SF method is shown in Figure 6. The τ values of large colloids were large and decreased with colloid concentration. At first glance, the concentration dependence of τ is peculiar because the relaxation times should remain constant irrespective of the concentration and even increase when the entanglement between

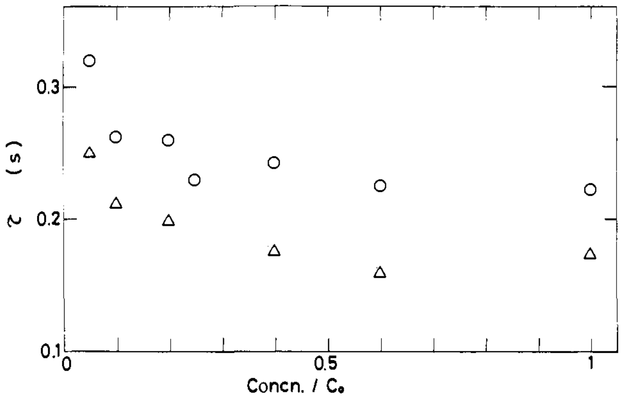

Figure 6. Concentration dependence of τ for tungstic acid colloid. (○) $2a$ = 300 Å, $2b$ = 8100 Å, $2c$ = 20 400 Å, c_0 = 0.05 wt %. (△) $2a$ = 140 Å, $2b$ = 7900 Å, $2c$ = 17 900 Å, c_0 = 0.063 wt %.

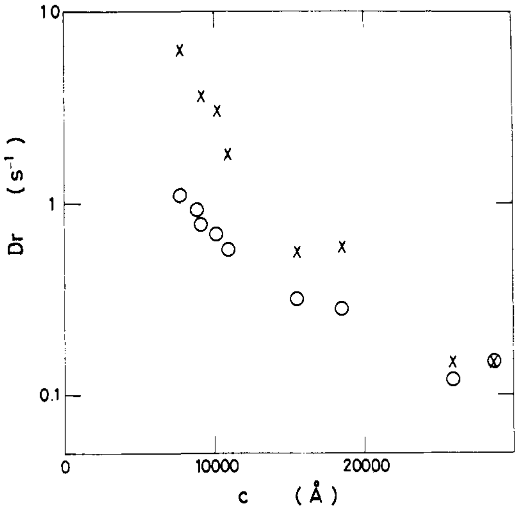

Figure 7. Comparison of D_r values observed and from the theory: (○) obsd, (×) calcd Perrin's equation.

colloids occurs in high concentrations. However, this observation can be explained by the enlarged effective size of the particle due to the Debye-screening-length (double layer thickness). The details of this effect will be discussed later.

The rotational diffusion constant, D_r, is obtained directly from the observed τ values by using eq 1. The D_r values thus observed

$$D_r = 1/6\tau \qquad (1)$$

are given in Figure 7 for various sizes of tungstic acid colloids. Crosses denote the values of D_r calculated from Perrin's equations (eq 2–5 below) for ellipsoidal colloids by using the crystallographic size.[29] The theoretical values of D_r of ellipsoids can be obtained from Perrin's equations without any assumptions if three axes (a, b, and c) are given

$$D_r = \frac{3kT(a^2P + b^2Q)}{16\pi\eta(a^2 + b^2)} \qquad (2)$$

$$P = \int_0^\infty \frac{ds}{(a^2 + s)\sqrt{(a^2 + s)(b^2 + s)(c^2 + s)}} \qquad (3)$$

$$a^2P + b^2Q + c^2R = \int_0^\infty \frac{ds}{\sqrt{(a^2 + s)(b^2 + s)(c^2 + s)}} \qquad (4)$$

$$P + Q + R = \frac{2}{abc}, \; a < b < c \qquad (5)$$

where a, b, and c denote the lengths of the minor, middle, and major axes of an ellipsoidal colloid. The constants P, Q, and R are derived from eq 3–5. k, T, and η in eq 2 are the Boltzmann constant, the absolute temperature, and the viscosity of the solvent, respectively.

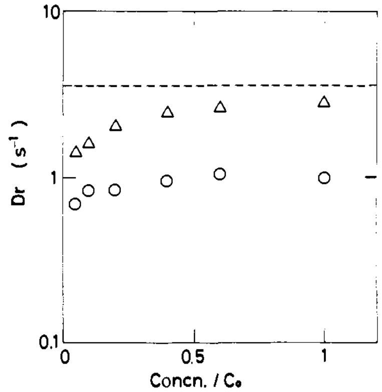

Figure 8. Comparison of D_r values observed and from the theory. Influence of Debye-length. c_0 = 0.063 wt %; (○) obsd, (△) calcd with Debye-length, (---) calcd with crystallographic size.

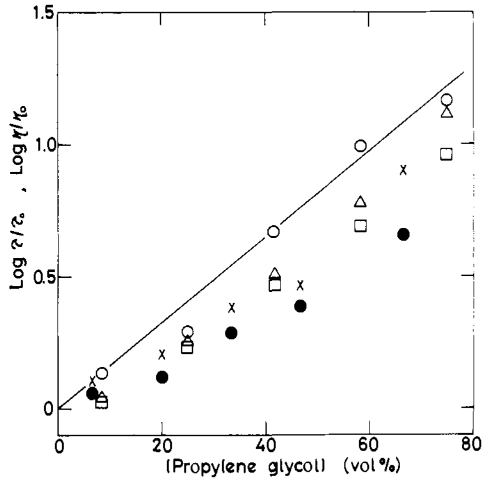

Figure 9. Influence of solvent viscosity on the rotational relaxation times of tungstic acid colloids. (○) log τ/τ_0, $2a$ = 370 Å, $2b$ = 15 200 Å, $2c$ = 31 300 Å, 0.023 wt %; (×) log τ/τ_0, $2a$ = 400 Å, $2b$ = 10 000 Å, $2c$ = 22 000 Å, ~0.03 wt %; (△) log τ/τ_0, $2a$ = 300 Å, $2b$ = 8100 Å, $2c$ = 20 400 Å, ~0.013 wt %; (□) log τ/τ_0, $2a$ = 140 Å, $2b$ = 7900 Å, $2c$ = 17 900 Å, 0.016 wt %; (●) log τ/τ_0, $2a$ = 100 Å, $2b$ = 6400 Å, $2c$ = 15 600 Å, 0.013 wt %; (—) log η/η_0.

The agreement of experimental and calculated values is surprisingly excellent, especially for the large colloids as can be seen in the figure. However, the observed values for the small particles were somewhat smaller than the calculated ones. Since the experiments were done in the absence of foreign salt, the Debye–Hückel double layer thickness (Debye-screening-length, D_l) given by $1/\kappa$ (κ is the Debye parameter) should be taken into account in the evaluaton of the effective size of the colloids; that is, the effective values of a, b, and c axes are $a + D_l$, $b + D_l$, and $c + D_l$, respectively

$$D_l = (4\pi Bn)^{-1/2} \qquad (6)$$

where B is the Bjerrum length ($e^2/\epsilon kT$, 7.19 Å at 25 °C) and n is the concentration of "free" cations and anions in solution. e and ϵ are the electronic charge and the dielectric constant of solvent, respectively. In the absence of foreign salt, n corresponds to the free counterions (protons). In Figure 8 the observed and theoretical values of D_r from the effective size including the Debye-length are compared. For spherical polymer latices, the fraction of free gegenions has been reported to be 0.10.[30–32]

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However, we have no information on the stoichiometric charge number on the surface of tungstic acid colloid. Thus, we estimated the amount of free protons from the solution conductance and from the reference values of equivalent conductance of protons. The evaluated D_l values for our system were in the range of several thousand angstroms. This correction term then became quite significant for the smaller colloids. The triangles in Figure 8 show the values of D_r calculated from Perrin's equation with use of effective semiaxes including Debye-length. The dashed line indicates the rotational diffusion constant estimated by using crystallographic size. The increasing tendency of D_r with concentration is clearly the same as that shown by the triangles, though the absolute values are slightly different. This deviation is believed to be due to the rough estimation of the amount of free protons.

The significance of the Debye-length has often been pointed out for the solution properties of various colloids and polyelectrolytes in salt-free systems such as the ordered solution structure in monodispersed latices,[33-37] conformation of ionic flexible polymers,[38-41] and very low mobility of spherical colloids at extremely low ionic strength.[42-44]

Next, we examined the viscosity effect of solvent on the relaxation times. In Figure 9 the relaxation times are given for the mixture of propylene glycol and water. τ and τ_0 are the relaxation times observed for the mixture and water, respectively. Five kinds of ellipsoidal colloids were used, of which $2c$ varies from 15 600 to 31 300 Å. The solid line shows log η/η_0 for the water–propylene glycol mixture, where η and η_0 stand for the viscosities of the mixture and pure water, respectively. Equations 1 and 2 tell us that τ should increase proportionally to the increase in the viscosity of solvent. The τ values increased with viscosity as is shown in Figure 9. However, the log τ/τ_0 term was slightly smaller than the log η/η_0 value especially for small colloids. This must be due to the significant contribution of the Debye-length discussed above, though a quantitative discussion is difficult because of the changes in the dielectric constant of the solvent mixture.

Conclusions

A new and convenient way of determining the rotational diffusion coefficient (D_r) was successfully achieved by the SP–SF and CSF techniques for the ellipsoidal colloids of tungstic acid. The significant contribution of Debye-screening-length to the D_r has been described, particularly in salt-free systems.

Acknowledgment. The author sincerely thanks Professor N. Ise of the Department for his encouragement throughout this work. Useful comments from Professor N. Imai of Nagoya University are also highly appreciated. This work was funded by the Kurata Foundation.

Registry No. Tungstic acid, 7783-03-1.

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Variation of the Heterogeneous Electron Transfer Rate Constant with Solution Viscosity: Reduction of Aqueous Solutions of $\mathrm{Cr^{III}(EDTA)^-}$ at a Mercury Electrode

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Received April 11, 1986

Abstract: The one-electron reduction of $\mathrm{Cr^{III}(EDTA)^-}$ at a mercury electrode was studied by an AC impedance technique in aqueous solutions of different viscosities (varied by addition of sucrose). The standard rate constant of the heterogeneous electron transfer, k^s_{cor} (corrected for diffuse double layer effects with experimentally measured parameters), showed a significant variation with solution viscosity. This viscosity dependence of k^s_{cor} in the kinetically limited region was interpreted in terms of the dynamic properties of the solvent. A reasonable correlation between k^s_{cor} and the solvent polarity term $(n_D^{-2} - \epsilon_s^{-1})$ could be obtained only when the preexponential factor was allowed to vary inversely with solution viscosity.

A variation of the rate constant for heterogeneous electron transfer (et) reactions (k^s) with solution viscosity was reported by our laboratory for $\mathrm{Fe(CN)_6}^{3-/4-}$ in water and ferrocene$^{0/+}$ in dimethyl sulfoxide, at a Pt electrode.[1] Although this dependence is not predicted by the classical description of et reaction at rates far from diffusion control,[2,3] more recent theoretical treatments suggest this correlation by emphasizing the role of solvent dynamics in the et processes.[4,5,6b,c] Generally, explicit studies of

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