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_1 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 $\log \eta/\eta_0$ 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 $\log \tau/\tau_0$ term was slightly smaller than the $\log \eta/\eta_0$ 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.

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

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Abstract: The one-electron reduction of $Cr^{III}(EDTA)^-$ 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 $Fe(CN)_6^{3-/4-}$ 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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the influence of solution viscosity on chemical reaction kinetics provide direct tests about the involvement of the solvent dynamics in the activation step, as viscosity is a measure of solvent mobility. Systematic experimental investigations of this type for heterogeneous et reactions at electrodes, to our knowledge, have not been carried out. We have been especially interested in the correlation of k^s with viscosity (or diffusion coefficient) because of its relevance to the active area of electron-transfer reactions in polymer films and the rates of these reactions in comparison to similar reactions in bulk solution.

The one-electron reduction of $Cr^{III}(EDTA)^-$ in weakly acidic aqueous solution (pH 5) was used to study the dependence of the standard heterogeneous rate constant on viscosity. We are particularly interested in aqueous systems, because water is a frequently used solvent in electrochemical studies and the needed physical properties are available for use in simplified expressions to estimate standard rate constants with the consideration of the effect of solvent dynamics[4a] (vide infra). The $Cr^{III}(EDTA)^-$ metal complex exhibits nernstian cyclic voltammetric behavior for the reduction $Cr^{III}(EDTA)^- + e \rightleftarrows Cr^{II}(EDTA)^{2-}$ at low scan rates with a half-wave potential, $E_{1/2}$, of -1.15 V vs. Ag/AgCl. It was selected as a test system because it shows well-defined outer-sphere et[7,8] has a heterogeneous rate constant in a range that is accurately measurable by AC techniques in the solutions studied, and it has a relatively low charge among species soluble in H_2O, which minimizes the electrostatic work-term effect on measured kinetics. The standard rate constants were obtained at a hanging mercury drop electrode (HMDE) in solutions in which viscosity was varied by adding different amounts of sucrose. A mercury electrode is especially useful in these studies, because the observed rate constant for double layer effects can be corrected by direct measurement of electrode surface properties in the same solutions. Moreover, the smooth and renewable surface of a mercury electrode makes it unlikely that any observed effects could be caused by partial blockage of the electrode surface, as might be invoked with a solid electrode. Sucrose was chosen as the additive not only because it is electrochemically inert in the potential region studied but also because it can be used to produce a large variation of solution viscosity accompanied by only minor changes of the static dielectric constant. Data on the physical properties of aqueous sucrose solutions are readily available.[9]

Experimental Section

Materials. $Na[Cr^{III}(EDTA(H_2O))]$ was prepared from reagent grade $Cr_2(SO_4)_3$ and ethylenediamine tetraacetatic acid disodium salt (Fisher Chemicals).[10a] Sucrose (Aldrich "Golden Label") was added to water (taken from a Milli-Q reagent water system) to vary solution viscosity. Na_2SO_4 (MCB reagent) was used as supporting electrolyte.

Apparatus. A Model 303 static mercury drop electrode (SMDE) (EG&G PARC, Princeton, NJ) was used as the working electrode for all electrochemical measurements. It was driven by a home-assembled power supply through cable connector J1 on the SMDE. The working electrode was thus a HMDE with the drop size switch selected at the "L" (large) setting to yield a drop area of 0.022 cm^2. The capillary of the HMDE was drawn out to a sharp tip to avoid possible frequency dispersion effects.[11] A KCl saturated Ag/AgCl electrode was used as the reference electrode and a mercury pool as the counter electrode. The reference electrode salt bridge was drawn to a fine tip and filled with KCl-saturated agar. The reference electrode tip was positioned about 2 mm from the HMDE surface.

DC voltammetric curves were obtained with a PAR Model 175 universal programmer, a PAR Model 173 potentiostat, and a Model 2000 X-Y recorder (Houston Instruments, Inc.). AC measurements were performed with an EG&G Model 5206 two-phase lock-in digital analyzer (with internal oscillator) and an $X-Y_1Y_2$ double channel recorder (Soltec Corp.). Standard capacitors (Hewlett Packard Model 4440B) and resistors (Leeds and Northrup, Co.) were used to calibrate the linearity of the lock-in amplifier.

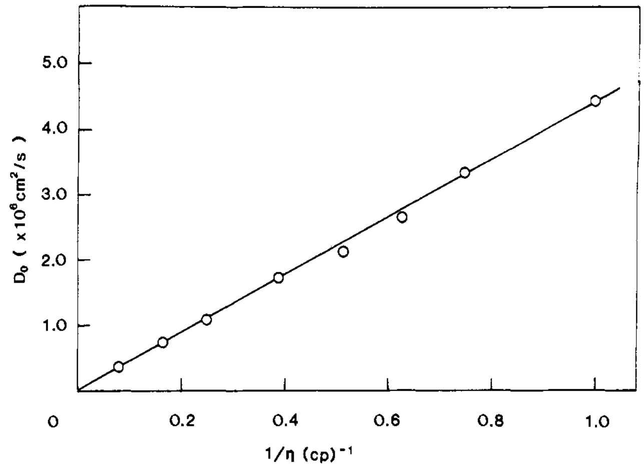

Figure 1. Plot of the diffusion coefficient, D_o, as a function of the reciprocal viscosity, $1/\eta$, for $Cr^{III}(EDTA)^-$ in aqueous 0.3 M Na_2SO_4 solutions containing different amounts of sucrose at 22 °C.

Procedure. Solutions of same supporting electrolyte concentration (0.3 M Na_2SO_4, pH 5) but with different viscosities were prepared by dissolving known amounts of sucrose. The diffusion coefficients of $Cr^{III}(EDTA)^-$, D_o, in these solutions were determined from DC cyclic voltammograms at potential scan rates (v) from 20 to 200 mV/s. Reversible behavior was observed under all conditions (separation of peak potentials of 60 mV), and diffusion coefficients were calculated from the slope of peak current, i_p, vs. square root of scan rate, $v^{1/2}$, plot.[12a]

The observed standard heterogeneous et rate constant, k^s_{ob}, was evaluated from AC impedance measurements[11,12b] at frequencies (f) of 100–3000 Hz. The in-phase and quadrature currents were recorded and analyzed to yield the total impedance of the cell at the DC half-wave potential, -1.15 V vs. Ag/AgCl for all solutions of different viscosity. The et coefficient, α, was assigned a value of 0.5, because the position of the AC voltammetry peak current was independent of frequency.[12b] (Yamada and Tanaka reported an α of 0.58 from their previous kinetic studies of the same compound.[8]) The conventional cotangent of phase angle, cot ϕ, vs. square root of AC frequency, $f^{1/2}$, plot was used to obtain k^s_{ob} (with the assumption that $D_o = D_R$). The correction for solution resistance and double layer charging capacitance were made analytically with a short computer program based on standard correction equations.[12b,13] The observed standard rate constants obtained for solutions of the same viscosity were reproducible to a standard deviation of 10%.

During the AC experiment, the phase angle shifted slightly when the sensitivity setting of the lock-in amplifier was changed. An external dummy cell, whose resistance was adjusted to a value comparable to that of the electrochemical cell, was used to set the phase angle to 0, and impedance measurements were performed at the same sensitivity setting.

All experiments were carried out at 22 ± 1 °C. The solutions were deoxygenated with prepurified argon gas. The bubbling and blanketing of the test solution with the gas was carried out for preset times with the SMDE apparatus.

Results

Diffusion Coefficients. A plot of the measured diffusion coefficients, D, vs. the reciprocal of the solution viscosity, $1/\eta$, is a straight line which intercepts the origin (Figure 1), as predicted by Stokes–Einstein equation

$$D = kT/6\pi r\eta \qquad (1)$$

where k is Boltzmann constant and r is the hydrodynamic radius of the diffusing species. The observed linear relation between D and $1/\eta$ shows that the radius of the solvated $Cr^{III}(EDTA)^-$, r_s, did not change with variation of the sucrose concentration. The

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Table I. Experimental Results for Solution Parameters and Rate Constants for the Reaction $Cr^{III}(EDTA)^- + e \rightarrow Cr^{II}(EDTA)^{2-}$ at a Mercury Electrode[c]

soln no.	sucrose concn (% by wt)	η[a] (cP)	D_0 (10^6 cm^2/s)	C_d (μf)	σ (μC/cm^2)	ϕ_2 (V)	k^s_{ob}[b] (cm/s)	k^s_{cor} (cm/s)
I	0	1.00	4.4	0.35	9.09	−0.044	0.45	5.9
II	4	1.11	3.9	0.44	10.09	−0.047	0.14	2.2
III	10	1.33	3.3	0.45	10.11	−0.048	0.084	1.4
IV	15	1.59	2.7	0.45	10.10	−0.048	0.065	1.1
V	20	1.94	2.2	0.45	10.08	−0.048	0.050	0.85
VI	26	2.57	1.7	0.45	9.96	−0.048	0.049	0.83
VII	34	4.04	1.1	0.45	9.69	−0.048	0.038	0.64
VIII	40	6.15	0.69	0.44	9.53	−0.048	0.029	0.49
IX	48	12.5	0.33	0.43	9.26	−0.048	0.021	0.35

[a] Data taken from ref 9. [b] Hanging drop mercury electrode (0.022 cm^2) at 22 ± 1 °C. $C_{Cr(EDTA)}$ = 3.75 mM. [c] The solution was 0.3 M Na_2SO_4, pH 5. Diffusion coefficient, D_0, differential double layer capacitance at dc reversible potential, C_d; observed standard rate constant, k^s_{ob}; and corrected standard rate constant, k^s_{cor} (made with measured charge density, σ, and potential at ohp, ϕ_2) in solutions of different viscosities, η, varied by adding sucrose to water.

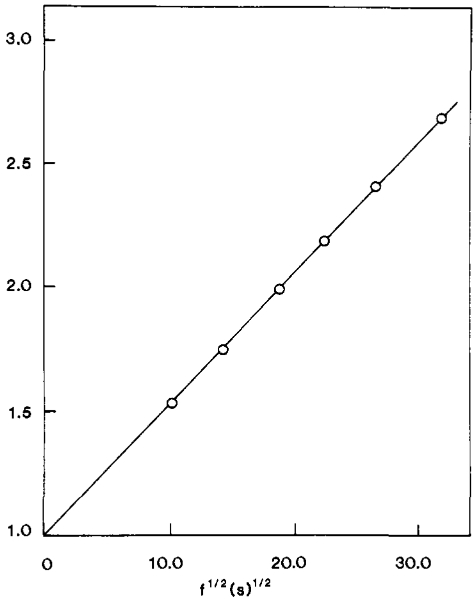

Figure 2. Plot of the cotangent phase angle, cot ϕ, as a function of the square root of AC frequency, $f^{1/2}$, for the reduction of $Cr^{III}(EDTA)^-$ at a mercury electrode in aqueous 0.3 M Na_2SO_4 + 20% sucrose, at 22 °C. Obtained from AC impedance measurements and corrected for the solution resistance and double layer charging capacitance.

r_s calculated from eq 1 is 4.9 Å. This hydrodynamic radius was used to estimate the free energy of activation for the et reaction (see eq 6).

Standard Rate Constant. Figure 2 is a typical plot of cot ϕ vs. $f^{1/2}$ for this system after correction for solution resistance and double layer capacitance. From these plots, the observed standard rate constants of the heterogeneous et reaction, k^s_{ob}, were obtained.[13] k^s_{ob} for the solutions of varying viscosity are collected in Table I. The rate constant decreased with an increase in solution viscosity, in a similar way to previously reported systems.[1]

With the assumption that electron transfer occurs at the outer Helmholtz plane (ohp), the observed rate constant can be corrected for the potential drop across the diffuse layer. The correction can be made by determining the potential at ohp, ϕ_2,[14]

$$k^s_{cor} = k^s_{ob} \exp[(z - \alpha n)F\phi_2/RT] \qquad (2)$$

where z is the charge of the reactant and k^s_{cor} is the corrected standard rate constant. According to the Gouy–Chapman–Stern model of the diffuse double layer, ϕ_2 is related to the charge density in the solution measured from ohp,[14,15] σ_s,

$$\sigma_s = [2\epsilon_0 \epsilon RT \sum_i C_i[\exp(-z_i F\phi_2/RT) - 1]]^{1/2} \qquad (3)$$

where ϵ_0 is the permittivity of free space (8.85 × 10^{-12} F/m), ϵ is the dielectric constant of the bulk solution, and C_i and z_i are the concentration and the charge (including sign) of the ith ionic species, respectively. The charge density at a given potential, E, was obtained from the measured differential double layer capacitance, C_d, by integration from the potential of zero charge, E_z to E:[14]

$$\sigma_s = \int_{E_z}^{E} C_d \, dE \qquad (4)$$

For the mercury electrode in an aqueous 0.3 M Na_2SO_4 solution, E_z was determined from electrocapillary measurements to be −0.45 V vs. SCE and was not changed significantly with the addition of sucrose.[13] Experimental values of σ_s at the DC half-wave potential in solutions of different viscosity are given in Table I. Also contained in Table I are ϕ_2's calculated from these experimentally measured σ_s values for each solution. They are virtually independent of the sucrose concentration over the region studied. The corrections of the rate constants for the potential drop across the diffuse layer were then made with these ϕ_2 values. These k^s_{cor} values are also listed in Table I.

Calculation of Rate Constant Based on Dielectric Continuum Theory. According to the classical treatment of outer-sphere et reactions, the standard rate constant is related to the activation free energy barrier, ΔG^*, by[2,3]

$$k^s_{cor} = \kappa_e A \exp(-\Delta G^*/RT) \qquad (5)$$

where κ_e is the electronic transmission coefficient and A the nuclear frequency factor. The activation free energy, ΔG^*, can be treated as the sum of two terms.[2,3] One refers to the inner reorganization energy of reactants, corresponding to the molecular structural changes of the reactant. The other refers to the solvent reorganization. For the reduction of $Cr(EDTA)^-$, the main contribution of ΔG^* is expected to be the solvent reorganization energy, ΔG^*_{os}; the inner reorganization energy, ΔG^*_{in}, is probably small according to the observed facile et behavior of the complex. We could not estimate ΔG^*_{in} from the bond length changes, because structural data for the $Cr(EDTA)^{2-}$ are not available. An attempt to grow a single crystal of $H_2Cr(EDTA)$ for an X-ray diffraction measurement was unsuccessful. A nonzero ΔG^*_{in} value for the homogeneous et reaction was estimated from a pseudoexchange study of $Cr(EDTA)^-$ in lutidene or acetate buffered solutions.[10b] This ΔG^*_{in} value probably does not apply under our conditions, because recent deuteron NMR results showed that the presence of acetate salt would likely convert the sexidentate EDTA complex to the quinquedentate one at this pH.[16] This change would strongly affect the ΔG^*_{in} value. In our present calculations of the total activation energies, ΔG^*_{in} was neglected to obtain the estimated rate constants. This neglect of the unknown, but probably small,

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Table II. Calculation of the Standard Rate Constant of Heterogeneous et Reaction in the Sucrose–Water System with Two Different Methods of Evaluating the Preexponential Factor[e]

soln no.	ϵ_s[a]	ϵ_{opt}[a] ($=n_D^2$)	$(1/n_D^2 - 1/\epsilon_s)$	τ_L[b] (ps)	k^s_{cal}[c]	k^s_{cal}[d]
I	79	1.78	0.550	0.45	1.2	3.9
II	78	1.79	0.545	0.51	1.3	3.6
III	77	1.82	0.537	0.63	1.5	3.3
IV	76	1.84	0.531	0.77	1.6	2.9
V	74	1.86	0.524	0.98	1.8	2.5
VI	72	1.89	0.516	1.36	2.0	2.0
VII	70	1.91	0.505	2.21	2.4	1.4
VIII	68	1.96	0.496	3.56	2.7	1.0
IX	65	2.00	0.483	7.73	3.2	0.55

[a] Data taken from ref 9. [b] Calculated longitudinal relaxation time, τ_L, from eq 9 and 10. [c] Calculated standard rate constants from eq 6 and 7. [d] Calculated standard rate constants from eq 6 and 8. [e] ϵ_s, static dielectric constant; ϵ_{opt}, optical dielectric constant; n_0 refractive index.

inner reorganization energy does not have a major effect on the discussion of the et reaction kinetics, which are focused on the effects of solvent dynamics (vide infra). In attempting to calculate absolute numerical values of the rate constants, this neglect would certainly introduce errors, depending upon the actual magnitude of $G^\ddagger_{in}$; similar uncertainties arise (e.g., uncertainties in reactant radii) and are often involved in such calculations. The solvent reorganization energy can be estimated from the solvation energetics of reactant, employing the Born model[2,3]

$$\Delta G^\ddagger_{os} = (Ne^2/32\pi\epsilon_0)(1/r - 1/2d)(1/\epsilon_{opt} - 1/\epsilon_s) \qquad (6)$$

where N is Avogadro's constant, e is electron charge, r is the radius of reactant (taken here as 4.9 Å as estimated from the D values and eq 1), d is the distance from electrode to the reaction layer, and ϵ_{opt} and ϵ_s are the optical and static dielectric constants, respectively. $\epsilon_{opt} = n_D^2$ for nonabsorbing liquids,[17,18] where n_D is the refractive index.

The nuclear frequency factor, A, has sometimes been estimated from the gas-phase collision number involving hard spheres, Z. In case of heterogeneous reactions[2,3,6a]

$$Z = (kT/2\pi m)^{1/2} \qquad (7)$$

where m is the molecular mass of reactant. By applying eq 6 and 7 to the present electrode reaction, the standard rate constants were calculated; these are listed in Table II for the different solutions. κ_e was taken to be unity with the assumption that the et reaction proceeds adiabatically.

Calculation of the standard rate constants was also made with the nuclear frequency factor obtained from the following equation:

$$A = K_p(1/2\pi\tau_L)(\pi\Delta G^\ddagger_{os}/RT)^{1/2} \qquad (8)$$

This equation has been derived by using the encounter preequilibrium model with inclusion of effects of solvent dynamics on the et reaction in polar media.[4,6c] The equation is applicable for weakly adiabatic et processes in "overdamped" solvents.[4a] In eq 8, K_p is the equilibrium constant of the precursor formation,[6a] and τ_L is the longitudinal dielectric relaxation time of the solvent, which is related to the Debye relaxation time, τ_D, by[17,18]

$$\tau_L = (\epsilon_\infty/\epsilon_s)\tau_D \qquad (9)$$

where ϵ_∞ is the dielectric constant at high frequency. For water, ϵ_∞ is ca. 4.3 at 25 °C (assigning $\epsilon_\infty = \epsilon_{mw}$).[18] Calculations of the standard rate constants based on eq 6 and 8 were performed by assigning $\kappa_e K_p = 6 \times 10^{-9}$ cm (assuming the et reaction is adiabatic only for the closest approach of the reactants to the electrode surface[6c,d]) and evaluating τ_D from the Debye equation[17,18]

$$\tau_D = 4\pi a^3\eta/kT \qquad (10)$$

where a is the radius of the H_2O molecule and η the viscosity of the bulk solution. The results obtained are also listed in Table II. In both calculations, the distance from the reaction layer to the electrode surface, d, was taken as infinite in eq 6, i.e., the image interaction between the reactant and the electrode at the transition state was neglected.[19]

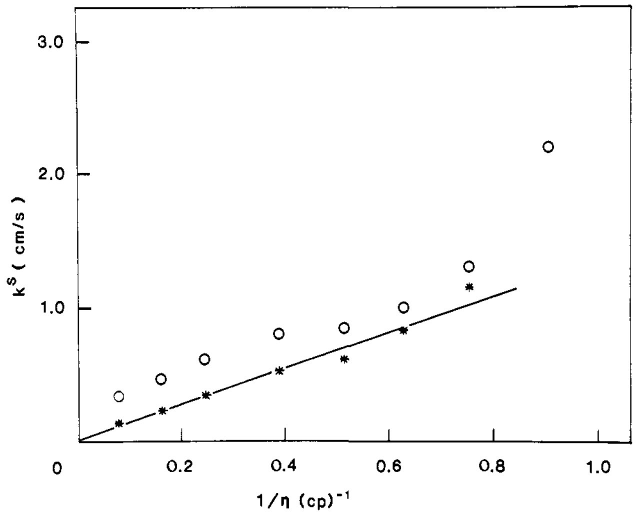

Figure 3. Plot of the double layer corrected standard rate constant of the heterogeneous et reaction, k^s_{cor} (circles), and the normalized standard rate constant, k^s_{norm} (stars), as a function of the reciprocal of the solution viscosity, $1/\eta$, for $Cr^{III}(EDTA)^-$ reduction at a mercury electrode in aqueous 0.3 M Na_2SO_4–sucrose solutions at 22 °C. Definition of k^s_{norm} is given in eq 11 with the reference solution: II (see text).

Discussion

Dependence of k^s_{cor} on η. After the double layer correction, based on experimentally measured parameters, k^s_{cor} was found to show a significant variation with solution viscosity (Figure 3). Since the rate of the et reaction was not near the diffusion-controlled region over the viscosity region studied, the dependence of k^s_{cor} on η reflects the importance of viscosity-related solution properties on the heterogeneous et kinetics. The interpretation of the dependence could be made on the basis of the influence of the solvent dielectric relaxation dynamics on the activation processes of the et reaction. As previously seen in eq 8, an important prediction drawn from this treatment is that the nuclear frequency factor depends inversely on the longitudinal dielectric relaxation time of the solvent. The longitudinal relaxation time can be estimated from eq 9 and 10. A dependence of k^s_{cor} on η is thus established. Estimation of the Debye relaxation time, τ_D, from the bulk solution viscosity, η, based on eq 10 is probably only a rough approximation for the present water–sucrose system. A correlation between τ_D and η, however, is expected. Previous experimental results actually show a systematic increase of the principal relaxation time of water with an increase in the concentration of various added nonelectrolyte materials.[18]

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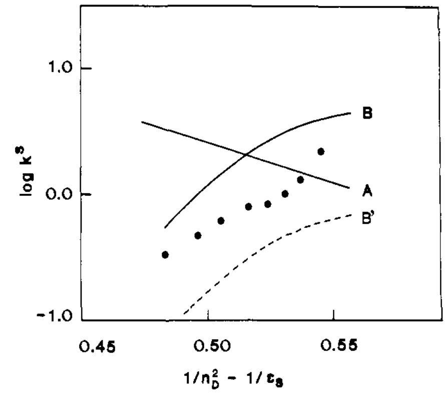

Figure 4. Plot of the standard rate constant of the heterogeneous et reaction, k^s, as a function of the solvent polarity term $(n_D^{-2} - \epsilon^{-1})$ for the reduction of $Cr^{III}(EDTA)^-$ at a mercury electrode in aqueous 0.3 M Na_2SO_4–sucrose solutions. Line A, calculated with eq 6 and 7; lines B and B′, calculated with eq 6 and 8 by assigning $\kappa_e K_p$ = 0.6 and 0.1 Å, respectively (see text); points are experimental results corrected for the double layer effect.

A dependence of the rate constant on viscosity has been explained for a more general case, an elementary chemical transformation reaction occurring in a solvent cage.[20] Basically, a dependence would be observed if the activation step for the passage of the reactants from initial to transition state not only requires energy for the reorganization of the medium but also is coupled to the dynamics of the reorganization processes. This requires that the relaxation time of the medium be longer than, or comparable to, the time the reaction complex stays in the transition state; this is probably the case for certain outer-sphere et reactions. A formula to estimate the nuclear frequency factor for chemical transformation reactions that involve changes in volume and/or shape of the reaction complex is very similar to eq 8,[20] which applied specifically to et reactions. The involvement of solvent dynamics in the kinetics of a chemical transformation reaction is determined by the relative value of the two time scales.

A dependence of standard rate constants of et reactions on viscosity can also be seen in recent studies of a series different solvents for both heterogeneous and homogeneous et reactions.[6c,21,22]

Comparison between k^s_{cor} and k^s_{cal}. To examine the applicability of the theoretical treatments of et reactions, a plot of the standard rate constant k^s vs. the solvent polarity term $(n_D^{-2} - \epsilon_s^{-1})$ is often used. Figure 4 is the plot for the present electrochemical system. Lines A and B are different calculated results based on eq 6 and 7 and eq 6 and 8, respectively. Although both calculations give similar estimated magnitudes for k^s, the manner by which k^s varies with $(n_D^{-2} - \epsilon_s^{-1})$ is different. The treatment that does not include the influence of solvent dynamics (line A) predicts a linear increase of ln k^s with a decrease of the quantity $(n_D^{-2} - \epsilon_s^{-1})$. This was not observed in the experiments. The experimental data showed an opposite trend, i.e, a decrease of ln k^s with an increase in solvent polarity. This trend matches the prediction drawn from the model that considers the effect of solvent dielectric relaxation dynamics on an outer-sphere et reaction (line B). Equation 8 applies well to the present system, because water is a solvent whose longitudinal relaxation time is longer than its thermal rotational time and in which the inertial effect may be negligible.[4,23] The results presented in Figure 4 do not rule out a correlation between k^s and $(n_D^{-2} - \epsilon^{-1})$ as suggested by eq 6. The observed rate constants did not increase with a decrease of solvent polarity probably because of the overriding influence of viscosity, since the polarity change was accompanied by a much greater change in solution viscosity.

A dotted line B′, calculated with the same equations as used for line B but assigning $\kappa_e K_p$ = 0.1 Å, was also drawn in Figure 4. With respect to the choice of K_p's, line B′ may be considered more internally consistent with line A than line B, because the preexponential factor for line A, given by eq 7, is less than 10^4 cm s^{-1}. This value can be rewritten as $\kappa_e K_p \nu$, where ν is a frequency factor for motion along the reaction coordinate. If $\nu \sim 10^{13}$ s^{-1}, as is often assumed, then $\kappa_e K_p \leq 0.1$ Å.[24] As is evident in Figure 4, for the present system, the calculated "solvation equilibrated" rate constant (line A) is larger than the calculated "solvent dynamic controlled" ones (line B′) in the solvent polarity region studied. Thus, based on these calculated results, the theory[5d] would also predict the reaction rate constant to follow the "solvent dynamic controlled" behavior as observed in the experiment.

When a line was drawn through the first eight points in the k^s_{cor} vs. $1/\eta$ plot, it did not intercept the origin (see Figure 3, circles). Better linearity and an intercept of zero were obtained for k^s_{norm} vs. $1/\eta$ (see Figure 3, stars). Here k^s_{norm} was defined as

$$k^s_{norm} = k^s_{cor} \exp[(\Delta G^\ddagger_{os} - \Delta G^\ddagger_{os}{}^\circ)/RT] \qquad (11)$$

where $\Delta G^\ddagger_{os}$ is the free energy barrier for the solution being considered and $\Delta G^\ddagger_{os}{}^\circ$ is the free energy barrier for a "reference solution", both calculated from eq 6. Since the free energy barrier only varies with solvent polarity according to eq 6, k^s_{norm} is actually the standard rate constant that would be obtained if the solvent polarity term, $(n_D^{-2} - \epsilon_s^{-1})$, was kept constant, at the value of the "reference solution". Thus, the variation of k^s_{norm} in solutions with different sucrose concentrations would reflect the viscosity dependence alone. The plot of k^s_{norm} vs. $1/\eta$ in Figure 3 suggests that the nuclear frequency factor $A = A'/\eta$ with $A' \sim 4 \times 10^3$ (cm·cP)/s for the present system. This inverse proportionality between A and η is also predicted by eq 8 along with eq 9 and 10.

Conclusion

Detailed experimental examination of the electrochemical kinetics for the reduction of $Cr^{III}(EDTA)^-$ in water–sucrose solutions at a mercury electrode reveals a significant variation of the heterogeneous et rate constant with solution viscosity. The observed variation can be explained by the involvement of solvent dielectric relaxation dynamics in the et processes, since the solvent relaxation time and viscosity vary in the same direction. Other factors, such as the reorientational dynamics of reactant coupled with the activation processes, may also contribute. Correlation between the experimental rate constants and the solvent polarity term $(n_D^{-2} - \epsilon_s^{-1})$, predicted by Marcus in the formula for the estimation of solvent reorganization free energy in an outer-sphere et reaction, eq 6, is reasonable, when the effect of viscosity on the preexponential factor is taken into account. The variation of rate constant on viscosity observed here for electrode reactions also holds for other types of chemical reactions.[20]

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Registry No. $Cr^{III}(EDTA)^-$, 16091-77-3; Na_2SO_4, 7757-82-6; $Cr^{II}(EDTA)^{2-}$, 12558-56-4; Hg, 7439-97-6; sucrose, 57-50-1.

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