

Enthalpy and Electrostriction in the Electron-Transfer Reaction between Triplet Zinc Uroporphyrin and Ferricyanide

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The electron-transfer reaction of triplet-state zinc uroporphyrin (ZnU) with ferricyanide ion, using pulsed, time-resolved photoacoustics, has a very large volume contraction of $-35 \pm 2 \text{ \AA}^3/\text{molecule}$ and an enthalpy change of $-1.5 \pm 0.15 \text{ eV/molecule}$. Via the known free energy of this reaction, $-1.31 \text{ eV/molecule}$, the $T\Delta S$ is $-0.2 \pm 0.2 \text{ eV/molecule}$ ($T = 25 \text{ }^\circ\text{C}$). The volume change is somewhat larger than that observed in bacterial reaction centers: the high charge of the ferri/ferrocyanides compensates for the much larger dielectric coefficient of water causing the electrostriction to be about the same. The classical Drude–Nernst equation predicts a volume change of about half the observed value. This failure for small or highly charged ions has been often noted in the literature. We partially account for this failure with a simple saturation function for the orientation polarization of the water dipoles in the electric field of the ions using the integral form of the Drude–Nernst equation. X-ray structural data show that the ions themselves do not change volume with change of charge. Electrochemical measurements show that the ferri- (+electron) to ferrocyanide reaction has a molar enthalpy of $-1.15 \pm 0.1 \text{ eV}$ and entropy ($T\Delta S$, $T = 25 \text{ }^\circ\text{C}$) of $-0.65 \pm 0.15 \text{ eV}$ at standard conditions versus the normal hydrogen electrode. Allowing for errors, we may assign the differences between the photoacoustic and electrochemical data to the $\text{ZnU} \rightarrow \text{ZnU}^+$ (+electron) partial reaction. Its enthalpy is $-0.35 \pm 0.2 \text{ eV}$ and $T\Delta S$ is $+0.45 \pm 0.35 \text{ eV}$ under the same conditions. Continuing in this manner, we can use the previously measured thermodynamic values for the triplet $\text{ZnU} + \text{naphthoquinone-2-sulfonate (NQS)}$ to obtain those for the partial reaction $\text{NQS (+electron)} \rightarrow \text{NQS}^-$. Its molar enthalpy is $-0.75 \pm 0.3 \text{ eV}$ and the $T\Delta S$ is $-0.7 \pm 0.4 \text{ eV}$. The entropy changes are clearly important contributions to the free energy. It is the unique ability of pulsed, time-resolved photoacoustics to easily obtain such thermodynamic data that renders it a most useful tool.

Introduction

The photoacoustic method has been used for high-sensitivity measurements in weakly absorbing and opaque media. The theory and early applications have been reviewed by Tam.¹ Time-dependent photoacoustics is now used in chemical systems where kinetic and thermodynamic data are to be measured. Both enthalpy and volume changes can be obtained for each time-resolved step of a photoinitiated reaction. Photoacoustic methods and their usage have been thoroughly reviewed.² The method has been applied to gain new insights into volume changes associated with excited-state electron-transfer reactions.^{3–5} In aqueous solutions these changes of reaction volumes can be separated from the thermal changes by conducting experiments near $4 \text{ }^\circ\text{C}$, where the thermal expansion of water is zero. Arata and Parson have used this effect in a study of bacterial reaction centers⁶ and Ort and Parson in a study of bacteriorhodopsin.⁷ Given the free energy of the observed reaction, measurement of the enthalpy leads to its apparent entropy.^{8,9}

The volume contraction on charge separation in the bacterial reaction centers is very large, $\sim 30 \text{ \AA}^3/\text{molecule}$.^{6,9–13} It is assigned to electrostriction enhanced by the low dielectric

coefficient of the surrounding protein. A very similar charge transfer between triplet zinc uroporphyrin and naphthoquinone-2-sulfonate (NQS) in water produces a volume contraction of only -4 \AA^3 .⁸ Since the electrostriction increases with the square of the charge on the ions (see below), it was expected that using a highly charged acceptor such as ferricyanide would increase the electrostriction. This would serve to both test this prediction quantitatively and, by use of the enthalpy and entropy change in the ferricyanide–ferrocyanide transition previously measured by electrochemical methods,¹⁴ to extend the measures to porphyrin and quinone components of these electron-transfer reactions. Photoacoustic measurements on multicharged ions have been carried out by Braslavsky and co-workers. In the reaction between excited Ru(bpy)_3^{2+} and ferric ion in acidic solution, only small volume changes were observed because of the symmetrical charge arrangement.⁴ That between the same donor and methyl viologen as acceptor resulted in a large volume expansion ($+17 \text{ \AA}^3$) as expected.⁵

The reaction to be studied here is that between triplet zinc uroporphyrin (^3ZnU) and ferricyanide (FeCN^{3-}) ion to form the porphyrin cation (ZnU^+) and ferrocyanide (FeCN^{4-}):



This reaction has been previously studied by flash photolysis,¹⁵ and the yield of ions was found to be $100 \pm 10\%$ under the

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presently used conditions. Analysis of the rate constants produced early evidence for electron transfer at a distance, i.e., tunneling, in solution.

Methodology

Only a sketch of the basic principles of photoacoustics is presented here since the details have been published.^{8,9} The volume change (ΔV_{th}) from heat released via the thermal expansivity and any other volume change (ΔV_{ch}) resulting from the absorbed light at each chromophore produce, via the compressibility of the solvent, a spherical pressure wave. At the speed of sound the components perpendicular to the back mirror (see Experimental Section) are convoluted over the cell volume to produce a plane wave which encounters the external detector and is converted to a time-dependent electrical signal by a piezo film. The photoacoustic signal is

$$S = (F/\kappa)(\Delta V_{\text{th}} + \Delta V_{\text{ch}}) = (F/\kappa) \sum (\alpha' q_i + \Delta V_i) \quad (2)$$

$$\alpha' = \alpha/C_p \rho$$

where F is the instrument sensitivity, κ the compressibility of the solution, α its thermal expansivity, C_p its heat capacity, ρ its density, q_i the heat evolved or absorbed in process i , and ΔV_i the volume change in process i . The sum is taken over all the reactions taking place.

The volume changes ΔV_i are assumed to be independent of temperature over the ~ 20 °C range used here, while the ΔV_{th} term is a strong function of the latter via the expansivity, α , of water. Instrument and solution parameters are calibrated by use of a reference solution, R, of identical absorbance as the sample but in which the absorbed photons are completely degraded to heat within the resolution time of the apparatus.

The quantities in eq 2 for a reaction at temperature T are normalized to those of the reference solution at a standard temperature, $T_R = 25$ °C. The values of α and κ ¹⁸ are then relative to those of the reference solution at T_R ; i.e., $\alpha_T = \alpha'(T)/\alpha'(T_R)$ and $\kappa_T = \kappa(T)/\kappa(T_R)$.

$$S(T)/S_R(T_R) = S_N(T) = (1/\kappa_T) \sum (\alpha_T q_i + \Delta V_i)/E \quad (3)$$

where subscript N stands for "normalized".

To obtain the sought-after energy and kinetic quantities, $S_R(T_R, t)$ is convoluted (*) with the time derivative of the assumed heat and volume change function $h_i(t)$ and fit to the measured $S_N(T)$. Dropping T and introducing t explicitly

$$S_N(t) = A_f S_R(t) + A_m S_R(t) * h'_i(t) + A_s \cdot 0 \quad (4)$$

Since the singlet to triplet transition is faster than the time resolution of our apparatus, the heat release appears as a step function and $h'_i(t)$ is the δ function. Hence, $A_f S_R(t) * h'_i(t) = A_f S_R(t)$. A_f represents the fraction of the excitation energy emitted in this process. From the second term (A_m), which describes the measurable time domain, one obtains the heat and volume changes of the electron-transfer reaction (eq 1). The number of terms depends on the reaction under study and the resolution, i.e., the signal-to-noise ratio of the experiment. These time-dependent changes will distort the signal as seen in Figures 3 and 4 of ref 8. In the present case of electron transfer between the excited Zn uroporphyrin and $\text{Fe}(\text{CN})_6^{3-}$ this distortion is exceptionally strong (Figure 1). Although the convolution yields a positive A_f , this positive peak is overshadowed by the negative signal of A_m indicating a large volume contraction. It is an

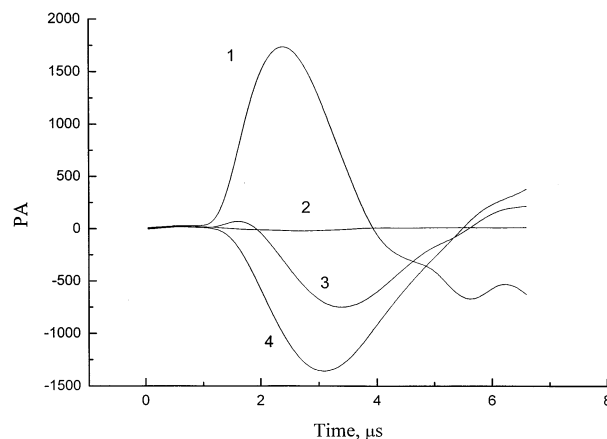


Figure 1. Photoacoustic (PA) signals for reaction 1 in H_2O . Lines 1 and 2: reference solution (Shaefter ink) at 24.7 and 2.1 °C. Lines 3 and 4: ZnU (0.2 mM) + FeCN_6^{3-} (1 mM) solutions at 24.7 and 2.9 °C. Excitation was at 532 nm, $50 \mu\text{J cm}^{-2}$. Average of 64 shots. PA scale arbitrary.

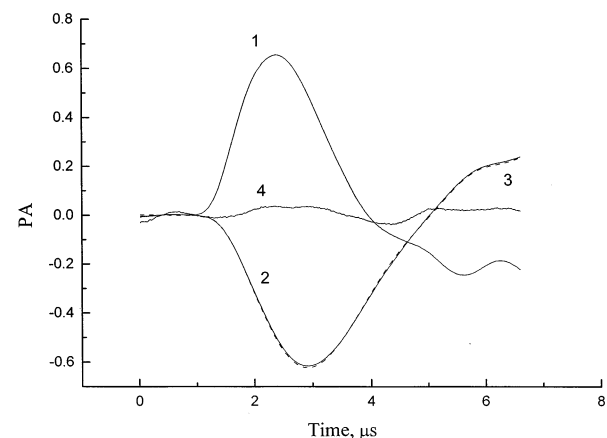


Figure 2. Convolution of PA signal of reaction 1 with reference in H_2O at room temperature. Line 1: reference at 24.4 °C. Full line 2: $\text{FeCN}_6^{3-} + ^3\text{ZnU}$ at 24.7 °C. Dashed line 3: Convolution of 1 to fit 2: $A_f = 0.26$, $\tau = 1.0 \mu\text{s}$, and $A_m = -0.93$. Line 4: residuals, scale $\times 5$.

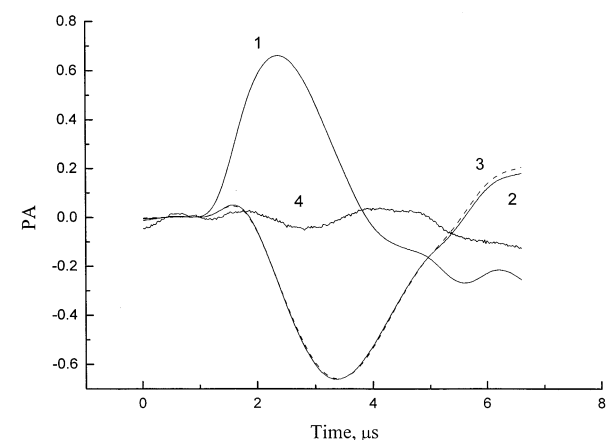


Figure 3. Convolution of PA signal of reaction 1 with reference solution in D_2O . Line 1: reference at 24.6 °C. Full line 2: $\text{FeCN}_6^{3-} + ^3\text{ZnU}$ at 4.9 °C, below T_m . Dashed line 3: convolution of 1 to fit 2 with $A_f = 0.22$, $\tau = 0.95 \mu\text{s}$, and $A_m = -1.88$. Line 4: residuals, scale $\times 5$.

example of the remarkable power of the convolution which is able to reproduce exactly (Figures 2 and 3) the complex experimental curve. The third term in eq 4 represents the slow ion recombination. For such a slow process the derivative h' tends to zero and thus $S_R * h'(t) = 0$.

Experimental Section

The apparatus is described in ref 3. A front face photoacoustic cell similar to that used by Arnaut et al.¹⁶ was used. The optical path was 1 mm, and the absorbance of the solution at the laser wavelength of 532 nm was $A = 0.35$.

The laser used was a Surelite Nd:YAG (Continuum) at its second harmonic, 532 nm. This photon corresponds to an energy, E , of 2.3 eV.

The backplate of the cell was a >99% reflective dielectric mirror Newport, BD.1. A 28 μm Kynar piezoelectric film behind the mirror made electrical contact with an Amtek 250 low noise amplifier. The other metalized film surface was grounded. The signal was channeled into a Tektronix RTD710 digitizer and thence to a HP340 computer for data acquisition and analysis.

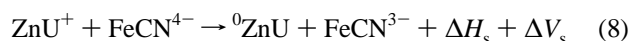
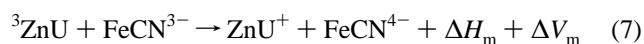
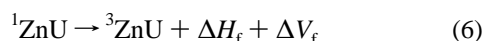
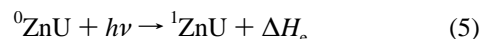
The Zn uroporphyrin (ZnU) was prepared from the flight feathers of Turaco birds¹⁷ and the reference was Shaeffer Jet Black ink. These and the $\text{K}_3\text{Fe}(\text{CN})_6$ (FeCN^{3-}) solutions were all in 0.025 M potassium phosphate buffer, pH 7.1. The ionic strength was $\mu = 0.14$. The ZnU concentration was about 0.15 mM, and the FeCN^{3-} concentration was 1 mM.

The reduction potential of Zn uroporphyrin in aqueous solution in 50 mM tetrabutylammonium tetrafluoroborate is 0.89 ± 0.02 V versus SHE.³ The solution containing ZnU and FeCN^{3-} was deoxygenated by bubbling prepurified humidified nitrogen (Matheson 99.999%) in a syringe connected to a three-way stopcock to either the solution or to the measuring cell. Measurements were taken at decreasing temperatures from 25 °C through the point of maximum density at T_m .

Results

The PA signal of the reference is positive (Figure 1) but that of the $^3\text{ZnU} + \text{FeCN}^{3-}$ is negative at 25 °C. A large volume contraction must offset the heat evolved on forming the triplet state and then the ions. At the temperature of maximum density, T_m , the PA signal of the reference is zero, but that of the reaction is yet more negative. Convolutions fit the data both at 25 °C (Figure 2) and below T_m (Figure 3). At room temperature the fast heat component is largely overshadowed by the large negative component, yet it is resolved from the slower volume contraction and the convolution fits the data very well. By convoluting $S_R(T)$ with $h'_i(t)$ (see eq 4) to fit the data $S_N(t)$ at differing temperatures, T , we obtain for each of the components i the coefficients $A_i(T)$ of eq 4. Plotting $\kappa_T A_i(T)$ versus α_T ¹⁸ results in a straight line of slope q_i/E (Figure 4). The value of $\kappa_T A_i(T)$ at $\alpha_T = 0$, i.e., at $\alpha(T_m)$, determines ΔV_i (eq 3) via α' at the standard temperature of 25 °C.

The reaction between triplet zinc uroporphyrin, (^3ZnU), and ferricyanide ion, (FeCN^{3-}), is described by the following steps:¹⁵



where the subscripts f, m, and s stand for fast, measurable, and slow and the superscripts 0, 1, and 3 indicate the ground, first excited singlet, and triplet states. The reactions of eq 5, excitation of ground-state ZnU to the singlet excited state, ^1ZnU , and subsequent relaxation to the lowest vibrational levels, are very

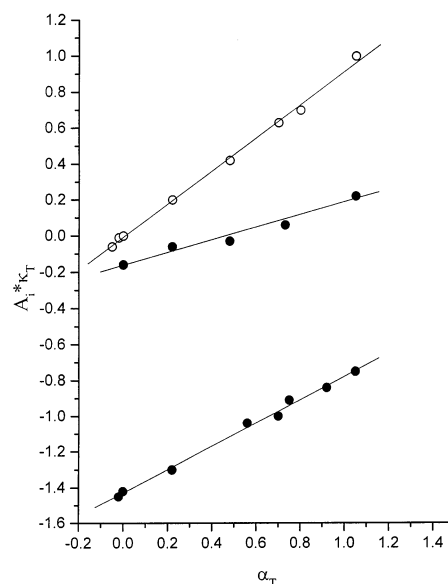


Figure 4. Plots of $A_i \kappa_T$ versus α_T for reaction 1 in H_2O . The slopes identify ΔH_f and ΔH_m , and the intercepts at $\alpha_T = 0$ identify ΔV_f and ΔV_m . Filled circles, upper line: A_f . Filled circles, lower line: A_m . Open circles: reference.

TABLE 1: Thermodynamic Parameters for the Reaction $^3\text{ZnU} + \text{FeCN}^{3-}$ in H_2O and in D_2O

	H_2O	D_2O
ΔH_f , eV	-0.6 ± 0.1	-0.6 ± 0.1
ΔH_m , eV	-1.5 ± 0.15	-1.45 ± 0.15
ΔV_f , \AA^3	-1.8 ± 1	-1.6 ± 1
ΔV_m , \AA^3	-34 ± 2	-37 ± 2
$k \times 10^9$, $\text{M}^{-1} \text{s}^{-1}$	1.1 ± 0.2	1.2 ± 0.2
T_m , °C	2.8	9.6

^a The data of ΔH_m and ΔV_m are corrected for a yield $\phi_f \phi_i = 0.9$. The rate constant is quoted at 25 °C.

fast and thus their ΔH terms are included in ΔH_f . The experimental results are summarized in Table 1.

The value of $\Delta V_f = -1.8 \pm 1 \text{ \AA}^3$ agrees with that previously found for the formation of triplet ZnU from the singlet.⁸ The value of ΔH_f agrees with the triplet yield of $\sim 95\%$ as has been found before.⁸ The measured ΔV_m yields a contraction of $-35 \pm 2 \text{ \AA}^3$ for the reaction of eq 7 in both H_2O and D_2O irrespective of their different α_T and T_m values. The slopes of plots such as Figure 4 produce a ΔH_m of -1.5 ± 0.15 eV for reaction 7 again independent of the hydrogen isotope. The temperatures for T_m for H_2O and D_2O in our buffer solutions of $\mu = 0.14$ are 2.8 and 9.6 °C, respectively. The added salts decrease T_m as expected.

The time constant and thus the second-order rate constant was $(1.1 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ at 0.14 ionic strength and 25 °C. It is less than the encounter limit because of charge repulsion. The activation energy, 0.27 eV, is somewhat larger than the activation energy of viscosity, 0.20 eV, again because of the (screened) repulsive charges of the reactants.

Since the volume change in this electron-transfer reaction is so large, any change of its magnitude with temperature will affect the derived value of ΔH . This possibility has been discussed in detail in ref 9, where it is shown that changes larger than 10% would be evident as nonlinearities in plots such as Figure 2. As an experimental verification of the constancy of ΔV , we ran the same reaction in D_2O , where T_m is ~ 10 °C instead of ~ 3 °C. The values of ΔH and ΔV remained the same (Table 1).

As a further test of the data analysis, we wrote a global convolution program which fits the data over the whole range of measurements, at six to eight temperatures, to eqs 3 and 4 with $\tau = 1/k$, ΔV_i , and ΔH_i as parameters determined by least-squares fit. The data in Table 1 are averages of the two analyses and fall within the estimated error range.

Discussion

Quantum Yields. The parameters measured by fits to the PA data are $\phi_i(\Delta V_f + \alpha'\Delta H_f)$ and $\phi_i\phi_t(\Delta V_m + \alpha'\Delta H_m)$, where ϕ_i is the triplet quantum yield and ϕ_t the yield of ions from the electron-transfer reaction. Since the energy gap between the excitation energy (2.3 eV) and the triplet energy (1.8 eV¹⁹) is 0.5 eV,²⁰ i.e.

$$\Delta H_f = \phi_t(0.5) + (1 - \phi_t)(2.3) \quad (9)$$

the measured ΔH_f of 0.6 eV implies a triplet yield (ϕ_t) of 0.95 ± 0.05 in agreement with our previous measurement.⁸ The ion yield (ϕ_i) of the $^3\text{ZnU} + \text{FeCN}^{3-}$ reaction measured by flash photolysis was 1.0 ± 0.1 .¹⁵ Thus the combined yield of ions is taken to be 0.9 ± 0.1 . We note that the lower quantum yield will have a direct effect on the true value of ΔV but far less effect on the true value of ΔH since it depends on an equation of the form

$$\Delta H_m = \phi_t\phi_i\Delta H(\text{true}) + (1 - \phi_t\phi_i)(-1.8) \quad (10)$$

where -1.8 is the energy difference between the triplet state and ground state of ZnU . Thus for the measured $\Delta H_m = -1.55$ eV, a yield of 0.9 gives $\Delta H(\text{true}) = -1.5$ eV and even a yield of 0.5 reduces it to only -1.2 eV. Thus only the value of ΔV will be affected beyond error by a lower yield of ions.

Volume Changes. The extraordinarily large negative amplitude of the PA signal on electron transfer from triplet ZnU to ferricyanide even at room temperature can confidently be ascribed to the increase of electrostriction on forming ferrocyanide ion from ferricyanide. The value observed for ΔV of this reaction, -35 \AA^3 , is much larger than that observed for the reaction of triplet ZnU with NQS,⁸ -4 \AA^3 . Thus most of the contraction arises from the change of ferri- to ferrocyanide. The difference in apparent molar volumes of these ions at $\mu = 0.1$ and 25°C is -48 \AA^3 .²¹

The thermodynamic description of electrostriction was given by Drude and Nernst²² some time ago. It is the pressure derivative of the free energy of a charged ion in a dielectric, or Born charging energy:

$$\Delta V_{\text{el}} = \partial \Delta G_{\text{el}} / \partial P = -(e^2/2\epsilon) (\partial \ln \epsilon / \partial P) (z^2/r) = (e^2\kappa/2\epsilon) (\partial \ln \epsilon / \partial \ln V) (z^2/r) \quad (11)$$

where ΔG_{el} is the Born charging free energy, P is pressure, e is the electric charge, κ is the compressibility $(-1/V) \partial V / \partial P$, V is the molar volume, ϵ is the dielectric coefficient, and z and r are the charge coefficient and radius of the ion. It is assumed that all parameters are independent of P and V . We use the this form of the equation because $\partial \ln \epsilon / \partial \ln V$ changes little ($\pm 20\%$) for the solvents for which data is available;²³ it is dimensionless, and its value is ~ -1 .

The Drude–Nernst (D–N) equation assumes the parameters are independent of pressure and volume and can be written as $\Delta V_{\text{el}} = -Bz^2/r$ with $B = 6.2$ for dimensions in angstroms in water. Thus, ΔV values of -15.5 \AA^3 for ferricyanide ion with radius 3.6 \AA and -28 \AA^3 for ferrocyanide are predicted. The difference, -12 \AA^3 , is far smaller than that measured from partial

molar volumes, -48 \AA^3 ,²¹ and that measured here, -35 \AA^3 . It has often been observed that the D–N equation fails for the case of small or highly charged ions.²⁴ Many hypotheses have been suggested for this failure (reviewed in refs 23 and 24). Note that a common suggestion, to have the radius of the ion be a function of pressure, is unlikely to be useful. If the radius of the ion is taken as the crystal or van der Waals radius, it is relatively incompressible because of the rapid increase of energy as filled orbitals interpenetrate. Liquids are much more compressible than crystals because of the few percent of “free volume” in a liquid. A better way to understand this failure of the D–N equation is that it is the parameters entered into the equation that are failing, not the equation itself. Being of thermodynamic origin, it is inherently correct in its integral form:

$$\Delta V_{\text{el}} = \int E^2(r) (\partial \epsilon / \partial P) 4\pi r^2 dr = (e^2/4\pi\epsilon_0) \int (\kappa/\epsilon) (\partial \ln \epsilon / \partial \ln V) / r^2 dr \quad (12)$$

where E is the electric field and the integral is taken from the radius of the ion, r_i , to infinity. Since κ decreases only by 20% at 1000 atm whereas ϵ decreases by a factor of 20 on freezing, the largest effect is the saturation of the dielectric coefficient by orientation polarization of the solvent dipoles in the strong field of the ion. Various authors have produced elaborations of this suggestion (reviewed by Millero²⁴) and complications which arise because of the Onsager reaction field and the interaction of the dipoles.²⁵ We suggest a very simple model. If the saturation is taken to follow the polarization of dipoles as given by the Langevin function

$$\epsilon = \epsilon_b - \Delta\epsilon(\coth x - 1/x) \quad (13)$$

where ϵ_b is the bulk solvent dielectric coefficient, $\Delta\epsilon = \epsilon_b - \epsilon_s$ with ϵ_s the saturated dielectric, and $x = Dez/4\pi\epsilon_0\epsilon_b kTr^2 = (r_0/r)^2$ with D the solvent dipole moment and other symbols having standard meanings. It is interesting that the value of r_0 defined by this equation is in fact of molecular dimensions. It is the average distance where the dipole and field interaction energy equals kT . For univalent ions in water at 25°C its value is 1.6 \AA . Then the integral in the Drude–Nernst equation becomes

$$\Delta V_{\text{el}} = (e^2\kappa z^2/8\pi\epsilon_0\epsilon_b r_0) (\partial \ln \epsilon / \partial \ln V) \int (dx/x) (1/(1 - (\Delta\epsilon/\epsilon_b)(\coth x - 1/x))) \quad (14)$$

where $x = (r_0/r)^2$. The term $\partial \ln \epsilon / \partial \ln V$ was chosen for its constancy (see above) and is removed from the integral. This is the density correction, and a more complete calculation would include it and the dependence of κ on pressure or density. Note that these corrections will decrease the magnitude of ΔV_{el} . Evaluation of the integral with Mathematica over a range of ionic radii limits of r_i/r_0 from 10 to 0.1 with $\Delta\epsilon/\epsilon_b = 0.95$ (i.e., $\epsilon_s = 4$) gave factors of 1–10 times the Drude–Nernst result of $1/r_i$. The factors increased sharply when $r/r_0 < 1$. This may be applicable to small ions such as Li^+ . Upper limits of r/r_0 between 100 and 1000 did not change these integrals.

We note that r_0 is proportional to \sqrt{z} (eq 13). If we assume $\epsilon_b = 80$ and $\epsilon_s = 4$, then $r_0 = 2.8 \text{ \AA}$ for ferricyanide and 3.2 \AA for ferrocyanide. The factors multiplying the Drude–Nernst result with $r_i = 3.6 \text{ \AA}$ are ~ 1.1 ; i.e., only a small effect is seen. Changing ϵ_s from 4 to 2 only increases the factor by about 3%. The increase is larger if $r/r_0 < 1$.

If the saturation is taken as the Brouillon function, which Danielewicz-Ferchmin²⁶ has argued is a better approximation

for dielectric saturation in hydrogen-bonded liquids:

$$\epsilon = \epsilon_b - \Delta\epsilon(\tanh x) \quad (15)$$

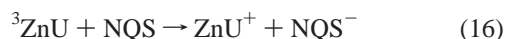
and the integral evaluated as above, assuming $\epsilon_b = 80$ and $\epsilon_s = 4$, then for ferricyanide with $r_o = 2.8 \text{ \AA}$ the factor is 1.4 and for ferrocyanide with $r_o = 3.2 \text{ \AA}$, it is 1.5. The difference in volumes then is -20 \AA^3 , lower than the measured apparent molar volume of -48 \AA^3 but closer to our -35 \AA^3 and an improvement over the simple Drude–Nernst result of -12 \AA^3 . The effect of the Onsager reaction field and interaction of the ordered dipoles may contribute to the smaller calculated value. The use of the tanh function for the saturation of the dielectric is useful for polar, hydrogen-bonded liquids as has been argued by Danielewicz-Ferchmin.^{25,26} We note that these corrections can be summarized as an “effective” ϵ to be substituted in the original D–N equation, eq 11. This effective ϵ depends on the ion size and charge in addition to bulk ϵ and its value at saturation.

There is the possibility that some of the observed volume contraction is in the ligands of the iron ions in addition to that of the surrounding water. To estimate this contribution we used the data on crystal structures of ferri- and ferrocyanides (CSD database,²⁷ version 531). Taking an example with univalent cations only, the averaged N–N distance is 6.195 \AA for dicesium ferricyanide (JIHPAR) and 6.223 \AA for lithium ferrocyanide (VUYBAS). The codes refer to the particular data set. Adding 1 \AA for the N orbitals, i.e., a radius of 3.6 \AA , the volume difference is $+2 \text{ \AA}^3$, i.e., an expansion. Thus we can safely assume that most of the electrostriction occurs in the surrounding water. The bound cyanide ions are already near maximally compressed by the charge on the ferric ion and the chemical bonding, as argued previously.

Charge separation in the bacterial photosynthetic reaction center shows a similarly large volume contraction, -28 \AA^3 .^{6,9–13} The smaller effective dielectric coefficient (~ 4)²⁸ of the protein surrounding donor and acceptor compensates for the decrease in magnitude of charge. We have shown that the volume contraction on photoexcitation of PSI in a cyanobacterium is also similarly large.²⁹

Enthalpy and Entropy. The fit of the data for the reaction ${}^3\text{ZnU} + \text{Fe}(\text{CN})^{3-} \rightarrow \text{ZnU}^+ + \text{Fe}(\text{CN})^{4-}$ with eq 7 produces $\Delta H = -1.5 \pm 0.15 \text{ eV}$ (Table 1). By the use of the energy of the triplet state, -1.8 eV ,¹⁹ the reduction potential of ZnU^+ , 0.89 V , and reduction potential of $\text{Fe}(\text{CN})^{3-}$, 0.40 V , at $\mu = 0.15$,¹⁴ the free energy of this reaction is: $-1.8 + 0.89 - 0.40 = -1.31 \text{ eV}$. Thus $T\Delta S$ is $-0.2 \pm 0.2 \text{ eV}$ ($T = 25 \text{ }^\circ\text{C}$). These values can be compared with the thermodynamic “half-cell” reactions determined electrochemically for ferricyanide (+electron) \rightarrow ferrocyanide: $\Delta H = -1.15 \pm 0.1 \text{ eV}$ and $T\Delta S = -0.65 \pm 0.15 \text{ eV}$.^{14,30,31} These are for standard conditions versus the normal hydrogen electrode (NHE) as are the ensuing reactions. The $T\Delta S$ value is an average of data which range from -0.78 to -0.52 eV , mostly due to varying assumptions as to the entropy of the NHE. The differences between our values and the literature values, assuming they are not simply errors, may be assigned to the triplet $\text{ZnU} \rightarrow \text{ZnU}^+$ (+electron) reaction. We obtain for it $\Delta H = -1.5 - (-1.15) = -0.35 \pm 0.2 \text{ eV}$ and $T\Delta S = -0.2 - (-0.65) = +0.45 \pm 0.35 \text{ eV}$.

For the reaction between triplet ZnU and naphthoquinone-2-sulfonate (NQS)



measured by photoacoustics,⁸ we obtained a ΔH of -1.1 eV and, via its ΔG of -0.85 eV (i.e., $\Delta G = -1.8 + 0.89 - 0.06$ (ref 32) $= -0.85 \text{ eV}$), a $T\Delta S$ of -0.26 eV . Hence, the reduction of NQS to NQS^- has a $\Delta H = -1.1 - (-0.35) = -0.75 \pm 0.3 \text{ eV}$ and a $T\Delta S = -0.25 - 0.45 = -0.7 \pm 0.4 \text{ eV}$. Since we are comparing reactions under similar standard conditions, the offset of the lesser known standard entropies cancels. However, we have increased the stated error to allow for the uncertainties in the standard entropies. The results highlight the importance of entropy in these reactions. Although obtainable through difficult and tedious electrochemical measurements, this thermodynamic information is uniquely easily available from studies with pulsed photoacoustics.

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