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Solvent Effects on Simple Electron Transfer Reactions. A Comparison of Results for Homogeneous and Heterogeneous Systems

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Solvent Effects on Simple Electron Transfer Reactions. A Comparison of Results for Homogeneous and Heterogeneous Systems

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Abstract

Solvent effects on the rate constants for both homogeneous and heterogeneous electron transfer reactions have been analyzed on the basis of current models which consider the role of dynamic relaxation processes in determining the magnitude of the pre-exponential factor. A statistical method for separating the effects of the solvent longitudinal relaxation time τ_L from those of the solvent permittivity parameter γ is described and applied to 15 sets of experimental data for which results are available in at least four solvents. The degree to which the explained variation in the logarithm of the rate constant could be attributed to either of these effects varied all the way from 0 to 100% depending on the degree of reaction adiabaticity and the relative sizes of the inner and outer sphere components of the free energy of activation. Data for the limiting cases in which there is no τ_L dependence in the pre-exponential factor or in which the pre-exponential factor is proportional to τ_L^{-1} were analyzed further to obtain the size-distance parameter and the components of the pre-exponential factor relevant to the encounter pre-equilibrium model. These parameters have been discussed with respect to current developments in electron transfer theory. Problems in estimating the longitudinal relaxation time in the solvent, required for the analysis, are also considered.

Introduction

The importance of solvent dynamical properties in electron transfer reactions has been recognized and elaborated in recent theoretical work [1-5]. At the same time, solvent effects on the kinetic parameters for simple electron transfer reactions involving molecular reactants and their corresponding monovalent cations or anions have been studied for both homogeneous [6-10] and heterogeneous processes [11-19] in a wide variety of solvents. Such systems are ideal for investigating solvent effects because work terms are a minimum, and the inner sphere free energy of reorganization is often much smaller than the outer sphere quantity. In earlier work, it was assumed that the solvent's primary role was an activational one, as expressed in the now famous Marcus dielectric continuum treatment [20]. Certainly, the first studies that considered a variety of solvents for homogeneous [6] and heterogeneous [11,21] processes showed that the early form of the equations for the rate constant in which the pre-exponential factor is not solvent dependent failed dramatically. This was in stark contrast with the results of intramolecular electron transfer processes for which excellent agreement was shown in many cases between charge-transfer band adsorption maxima, and the quantity predicted from electron transfer theory [22]. These studies offer very strong evidence for the general validity of the Marcus treatment [20] in so far as the activation process is concerned. Inspired by the recent theoretical work, more effort has been expended in understanding the role of the solvent in determining the pre-exponential factor [7-10,12,14-19] in the rate constant for intermolecular electron transfer. The evidence is now quite clear that both homogeneous and heterogeneous kinetic data correlate quite well with solvent relaxation times [15,17,23]. However, the precise functional dependence of the electron transfer rate constant on solvent relaxation time is by no means clear at the present time. Early work by Zusman [1] predicted that the pre-exponential factor in the rate expression is proportional to τ_L^{-1} where τ_L is the longitudinal relaxation time. Recent work by Marcus [5,24] has shown that Zusman's formulation is a limiting case, such that, as the inner sphere

reorganizational energy increases, the nuclear frequency factor ν_n should acquire a fractional dependence on τ_L^{-1}; that is, ν_n is proportional to $\tau_L^{-\alpha}$ where α is a fraction between 0 and 1. In addition, if the reaction is weakly adiabatic, one also expects the dependence of the pre-exponential factor on τ_L^{-1} to be weakened such that for non-adiabatic processes the solvent dependence of the pre-exponential factor disappears [25,26].

With much of the attention focussed on solvent dynamical effects, we were interested in determining whether the Marcus dielectric continuum model for the outer sphere reorganizational energy can be tested for simple electron transfer reactions using kinetic data obtained in a number of solvents. In a recent paper [27], we analyzed data for solvent effects on electrochemical rate constants on the basis of the limiting form of the solvent dependence of the pre-exponential factor ($\alpha = 1$), and found that the reorganizational free energy of activation depends on the solvent's dielectric properties in a manner predicted by electron transfer theory [20]. As a result of our analysis, it was possible to assess other parameters relevant to electron transfer theory such as the size-distance parameter which determines the magnitude of the activation energy, and the parameters for precursor complex formation. Another important test of electron transfer theory involves a comparison of kinetic data for homogeneous and heterogeneous electron transfer. Such a comparison necessarily involves assessing the role of imaging in determining the magnitude of the size-distance parameter for the heterogeneous process. One also needs a way of assessing the importance of solvent dynamical effects in determining the pre-exponential factor. In the present paper, we extend our previous analysis [27] to determine the importance of solvent dynamical effects in the kinetic data and compare results for homogeneous and heterogeneous reactions using data presented in the literature.

Theory and Analysis

According to Marcus' theory for electron transfer reactions [20,28,29], the rate constant for electron transfer, k_r, may be written

$$k_r = \kappa Z \exp(-\Delta G^*/RT) \qquad (1)$$

where κ is the electronic transmission coefficient, Z, a collision frequency and ΔG^*, the reorganizational free energy of activation. It is understood, in the present case, that the term Z contains any electrostatic work terms associated with bringing the reactant or reactants to the reactant site, so that the activation free energy is composed of two terms, ΔG^*_{is}, the inner sphere contribution due to internal structural reorganization, and ΔG^*_{os}, the outer sphere contribution from the solvent medium. ΔG^*_{is} can be estimated from the bond coordinate changes between the oxidized and reduced forms of the reactant, and the corresponding bond force constants which can be determined from vibrational spectroscopy [28,29]. The outer sphere quantity ΔG^*_{os} for homogeneous bimolecular reactions is given by [20,29]

$$\Delta G^*_{os} = \frac{N_O e^2}{16\pi\varepsilon_O}\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R_h}\right)\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right) \qquad (2)$$

where N_O is Avogadro's number, e, the electronic charge, ε_O, the vacuum permittivity, a_1, and a_2, the radii of the two reactants represented as spheres, R_h, their separation in the encounter complex, and ε_{op} and ε_S, the optical and static dielectric constants of the solvent, respectively. Since we are concerned here with reactions involving a molecule, and its corresponding cation or anion, $a_1 = a_2 = a$, and the size-distance parameter in eq. (2) reduces to $(a^{-1} - R_h^{-1})$. The corresponding value of ΔG^*_{os} for heterogeneous or electrochemical reactions is

$$\Delta G^*_{os} = \frac{N_O e^2}{32\pi\varepsilon_O}\left(\frac{1}{a} - \frac{1}{R_e}\right)\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right) \qquad (3)$$

where R_e is the distance between the reactant and its image in the conducting electrode.

These expressions for ΔG^{*}_{os} are based on the Born model for ion solvation, and hence, inherit some key assumptions, namely, that the solvent is a structureless continuum and that there is no spatial dispersion of the dielectric permittivity at distances beyond the reactant radius.

In its original form, the Marcus expression [20] for the homogeneous rate constant treated the pre-exponential factor in a 'gas phase' manner as an effective collision frequency, Z_h. When one includes the work term, the expression for Z_h may be written

$$Z_h = 4\pi N_O R_h^2 \left(\frac{RT}{2\pi M}\right)^{1/2} \exp(-w_h/RT) \qquad (4)$$

where w_h is the electrostatic work done to bring the reactants to the reaction site and M is the reduced mass of the reactants. In the case of heterogeneous processes, the collision frequency was written as

$$Z_e = \left(\frac{RT}{2\pi M}\right)^{1/2} \exp(-w_e/RT) \qquad (5)$$

where w_e is the electrostatic work done to bring the reactant to the reaction site near the electrode and M is now understood to be the mass of the reactant.

On the basis of the more recent encounter-preequilibrium model [25], the pre-exponential factor in equation (1) has been recast as $\kappa K_p \nu_n$ where K_p is the equilibrium constant for precursor complex formation and ν_n, the nuclear frequency factor giving the effective frequency with which the system crosses the free energy barrier. In the case of homogeneous electron transfer [25], the equilibrium constant K_p is given by

$$K_p = 4\pi N_O R_h^2 \delta r \exp(-w_h/RT) \qquad (6)$$

where δr is the range of reactant separations over which electronic coupling is sufficient for reaction. The corresponding equation for a heterogeneous process [30] is

$$K_p = \delta r \exp(-w_e/RT) \qquad (7)$$

The magnitude of δr which is important in determining K_p for both cases is considered to vary between 0.2 nm for adiabatic reactions to 30 pm for non-adiabatic reactions [31]. It should be noted that the formulation for the pre-exponential factor used here does not explicitly include the nuclear tunnelling factor [25,31] which can be assumed equal to unity for most electron transfer reactions at room temperature.

In general, the nuclear frequency factor ν_n depends on both internal vibrational and external solvent fluctuation frequencies for the reactant(s). A convenient way of expressing ν_n is in terms of a weighted average of frequencies associated with inner sphere vibrations, ν_{is} and outer sphere solvent reorientation, ν_{os}, that is [25,31],

$$\nu_n = \left(\frac{\nu_{is}^2 \Delta G^*_{is} + \nu_{os}^2 \Delta G^*_{os}}{\Delta G^*_{is} + \Delta G^*_{os}} \right)^{1/2} \tag{8}$$

In the limit that ΔG^*_{os} is much greater than ΔG^*_{is}, this reduces to $\nu_n = \nu_{os}$. Furthermore, it has been shown [1-4] for adiabatic reactions that under these conditions

$$\nu_n = \frac{1}{\tau_L} \left(\frac{\Delta G^*_{os}}{4\pi RT} \right)^{1/2} \tag{9}$$

where τ_L is the longitudinal or constant charge relaxation time [32]; τ_L is related to the Debye relaxation time τ_D through the expression

$$\tau_L = \tau_D \frac{\varepsilon_\infty}{\varepsilon_s} \tag{10}$$

where ε_∞ is the 'infinite frequency' dielectric constant. The quantity ε_∞ is regarded differently by different authors, some [5,33] defining it as the optical dielectric constant ε_{op} (n^2 where n is the refractive index) and others [16-18] as the value in the infrared frequency range. This problem will be addressed further below. Finally, in the limit that ΔG^*_{is} is much greater than ΔG^*_{os}, ν_n is equal to ν_{is} and the solvent dependence of the pre-exponential factor disappears [5,24].

A criterion for determining whether solvent dynamical frequencies should predominate in the pre-exponential factor of eq. (1) was given by Ovchinnikova [3,13] ; accordingly , eq. (9) is valid if the following condition is met:

$$\nu_{is} [\Delta G^*_{is}/(\Delta G^*_{is}) + \Delta G^*_{os})]^{1/2} \exp (-\Delta G^*_{is}/RT) > \tau_L^{-1} \quad (11)$$

Certainly, many systems are not expected to fulfill this criterion. Recent work by Nadler and Marcus [24] predicts that, as ΔG^*_{is} increases relative to ΔG^*_{os}, the rate constant k_r assumes a power law dependence on τ_L such that it is proportional to $\tau_L^{-\alpha}$ where α is a fraction between 0 and 1. On the basis of this work, a general way of writing eq. (1) for adiabatic reactions with inclusion of solvent dynamical effects in the pre-exponential factor is

$$k_r = A \tau_L^{-\alpha} \exp (-\Delta G^*/RT) \quad (12)$$

where the parameter A is equal to $\kappa K_p \nu_{is}$ when $\Delta G^*_{is} >> \Delta G^*_{os}$, and to $\kappa K_p \nu_{os}$ when $\Delta G^*_{os} >> \Delta G^*_{is}$, and the parameter α is a fraction between 0 and 1. The same expression may be used for weakly adiabatic reactions for which the coefficient α is expected to decrease from unity with departure from adiabaticity [26]. Rewriting eq. (12) making use of the expressions for ΔG^*_{os} given above, one obtains the result

$$\ln k_r = \ln A - \frac{\Delta G^*_{is}}{RT} - \alpha \ln \tau_L - g \gamma \quad (13)$$

In this equation, γ is the permittivity parameter given by

$$\gamma = \left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right) \quad (14)$$

and the quantity 'g' is defined for homogeneous reactions by

$$g_h = \frac{N_o e^2}{16\pi\varepsilon_o RT} \left(\frac{1}{a} - \frac{1}{R_h}\right) \quad (15)$$

or for heterogeneous reactions by

$$g_e = \frac{N_o e^2}{32\pi\varepsilon_o RT} \left(\frac{1}{a} - \frac{1}{R_e}\right) \quad (16)$$

It follows that one may assess the relative importance of solvent effects in the pre-exponential factor and in the outer sphere free energy barrier by performing a two parameter least squares analysis of the dependence of $\ln k_r$ on $\ln\tau_L$ and γ. Strictly speaking, the quantity lnA depends on γ for adiabatic reactions with $\alpha = 1$; however, this dependence correlates well with γ as will be shown below, so that the analysis of solvent effects on the basis of eq. (13) provides an excellent method of assessing the relative importance of the two contributions. It should also be kept in mind that the parameter α can change with solvent nature for a given reaction [24]. Thus, when α is determined by a least squares fit of eq. (13) to experimental data, the result obtained should be regarded as an average value especially when it is not at either of the limiting values (0 or 1).

In the limit that inner sphere reorganization energy dominates ($\alpha = 0$), the expression for the rate constant becomes

$$\ln k_r = \ln \kappa K_p \nu_{is} - \frac{\Delta G^*_{is}}{RT} - g\gamma \qquad (17)$$

Thus, the logarithm of the rate constant should be linear in the permittivity parameter γ, the size distance parameter being obtained from the slope, and the pre-exponential factor from the intercept provided the value of ΔG^*_{is} is known. Such a plot was used by Grampp and Jaenicke [7] to analyze the solvent dependence of kinetic data for electron transfer involving diaminobenzenes and their cation radicals. In the case that the outer sphere reorganization energy dominates and $\alpha = 1$, it can be shown [23,27] using eqs. (9) and (12) that

$$\ln\left(\frac{k_r\tau_L}{\gamma^{1/2}}\right) = \ln\left[\kappa K_p \left(\frac{g}{4\pi}\right)^{1/2}\right] - \frac{\Delta G^*_{is}}{RT} - g\gamma \qquad (18)$$

It follows that a plot of $\ln (k_r\tau_L/\gamma^{1/2})$ against γ should be linear with a slope of -g. Furthermore, if ΔG^*_{is} can be estimated from spectroscopic data, one may estimate κK_p from the intercept of such a plot [27]. It should be pointed out that eq. (14) assumes that if the reaction is adiabatic, the degree of donor-acceptor electronic coupling has not reduced the barrier height or altered the barrier geometry significantly [4, 47].

The analysis used here has only been applied to data obtained in aprotic solvents. Most protic solvents exhibit multiple relaxations, and there is some theoretical justification to define the longitudinal relaxation time in terms of the optical dielectric constant rather than the infrared value [5]. Indeed, Opallo [17] has shown clearly a difference in the way heterogeneous kinetic data for aprotic and protic solvents correlate with the value of τ_L. Obviously, the model for these protic solvents must be more complex than that presented above, and therefore, they are not considered in the present paper. Values of τ_L and γ for the solvents involved in the following analyses are given in Table I. The sources of the original data and values of ε_s, ε_{op}, ε_∞ and τ_D are tabulated elsewhere [34]. For the solvents considered, the longitudinal relaxation time varies from 0.2 to 8.8 ps, that is, by a factor of 50. On the other hand, the permittivity parameter varies by much less, and falls within the range 0.28 to 0.53. It should be noted that homogeneous electron transfer data [7,8] have been reported in solvents with quite small values of the permittivity parameter γ. When solvents with low dielectric constants contain an electrolyte, they have dielectric relaxation characteristics with multiple relaxations due to ion pair formation [35]. However, the data reported in such solvents and used below were obtained in the absence of supporting electrolyte [7,8]. Finally, the analyses represented by eq. (13), (17), and (18) should strictly speaking be applied to kinetic data which have been corrected for the work terms introduced here in the equilibrium constant K_p (eqs. (6) and (7)). The work terms are normally estimated on the basis of the extended Debye-Huckel theory for ionic strength effects in the case of homogeneous processes [25], or the Gouy-Chapman model for double layer effects in the case of heterogeneous processes [34]. Since discussion below for homogeneous reactions is limited to systems in which one of the reactants is uncharged, w_h is zero. The work term for heterogeneous electron transfer, w_e, is always non-zero within the context of the Frumkin model for double layer effects [36,37]. It has been argued in several studies [15-18] that double layer effects are negligible for the heterogeneous reactions considered. This subject is discussed in more detail below.

Results and Discussion

The dependence of the rate constant for electron transfer on solvent was analyzed on the basis of data for both homogeneous and heterogeneous systems which have already appeared in the literature using the equation

$$\ln k_r = \ln k_{ro} - \alpha \ln \tau_L - g\gamma \tag{19}$$

In this equation which follows directly from eq. (13) above, the parameter k_{ro} may be regarded as the solvent independent part of the rate constant. The coefficients α ad g as well as the normalized partial regression coefficients $\bar{\alpha}$ and $\bar{g}$ [38, 39] were determined by a least squares fit of the experimental data using the values of τ_L and γ summarized in Table 1. The partial regression coefficients α' and g' are defined by the equations [38, 39]

$$\alpha' = |\alpha| \left(\frac{\sum_i (\ln \tau_{Li} - \langle \ln \tau_L \rangle)}{\sum_i (\ln k_{ri} - \langle \ln k_r \rangle)} \right)^{1/2} \tag{20a}$$

and

$$g' = |g| \left(\frac{\sum_i (\ln \gamma_i - \langle \gamma \rangle)}{\sum_i (\ln k_{ri} - \langle \ln k \rangle)} \right)^{1/2} \tag{20b}$$

where $\langle \ln \tau_L \rangle$, $\langle \gamma \rangle$, and $\langle \ln k_r \rangle$ are average values of the quantities $\ln \tau_L$, γ, and $\ln k_r$, respectively, and the summation is performed over the parameters involved for the solvents used in a given set of experimental data. Since α' and g' are on the same scale, comparison of these parameters allows one to assess the relative importance of $\ln \tau_L$ and γ in determining the observed solvent effect. The normalized partial regression coefficients defined by the equations

$$\bar{\alpha} = \frac{\alpha'}{\alpha' + g'} \tag{21a}$$

and

$$\bar{g} = \frac{g'}{\alpha' + g'} \tag{21b}$$

give a direct estimate of the fraction of the variation in ln k_r with solvent explained by eq. (19) which can be attributed to variation in ln τ_L and γ, respectively. Although the actual value of α is important in assessing a given set of data and is reported in the following tables, very little significance can be attached to the value of g obtained in this analysis especially when α is close to or equal to unity. This follows from the fact that the parameter A in eq. (13) depends on $\gamma^{1/2}$ when $\alpha = 1$, and that there is a strong correlation between ln $\gamma^{1/2}$ and γ in the range of this parameter for the solvents considered (see Table 1). Thus, one could not carry out a four parameter least squares fit with ln $\gamma^{1/2}$, γ, and ln τ_L as independent variables. It follows that the value of g obtained in a fit of eq. (19) to experimental data does not just reflect the size-distance parameter when α is close to unity.

The results of fitting eq. (19) to data for homogeneous electron transfer are summarized in Table 2. Of the eight systems considered, the four diaminobenzene systems can clearly be considered to have very small dependence on τ_L. *In fact,* Grampp and Jaenicke [7] concluded that the inner sphere reorganization energy predominated for these systems and analyzed the solvent dependence on the basis of eq. (17). Although the number of solvents studied was not large, the quality of the fit is excellent as reflected by the high values of the regression coefficient. In the case of cobaltacene (CB) and ferrocene, the value of α is intermediate lying close to 0.5. Since these systems have low values of ΔG^*_{is} [10], this result may indicate that the reactions are weakly adiabatic. In the case of the cobaltacene system, the quality of the fit was not high when data for all eleven solvents were considered. However, when data for outlying points (BN and AC) were removed, the value of the regression coefficient increased markedly. This could be taken as evidence that the coefficient α is changing with τ_L since these solvents lie and the ends of the range of values of τ_L considered in these experiments [10]. On the basis of the partial regression coefficients, it is clear that 50 to 60% of the observed dependence of the logarithm of the rate constant on solvent can be attributed to variation in ln τ_L. For tetracyanoquinodimethane (TCQM) and decamethylcobaltacene (DMCB), the value of α is unity within experimental

error which indicates that these systems can be treated as adiabatic with a dominating contribution to the free energy of activation from outer sphere reorganization. In the case of the TCQM system, this conclusion was reached earlier by Harrer et al. [23] who first proposed the analysis of data for such systems on the basis of eq. (18). The results obtained show clearly that the solvent contribution to the free energy barrier makes up close to 40% of the explained solvent dependence so that analytical methods used to separate the pre-exponential solvent dependent factors from the exponential ones should be designed to avoid assumptions about the size-distance parameter.

Results of heterogeneous kinetic studies of solvent effects are summarized in Table 3. For these systems, a wide variation in the α parameter is also seen with error estimates much larger than for homogeneous systems with the same number of solvents. In the case of the heterogeneous process, the net change in the rate constant with solvent is smaller, so that the quality of the fit is not expected to be as good as for the corresponding homogeneous system given the same number of solvents and the same range of the parameters γ and $\ln \tau_L$. For the metal sandwich compounds, α is unity within experimental error, and the majority of the solvent dependence can be attributed to the τ_L dependence of the pre-exponential factor. These reactions are the fastest of those considered in Table 3, and were chosen to investigate solvent effects because they possess low inner sphere reorganization energies [16,18]. In the case of phenothiazine and 1,4-diaminobenzene (DAB) intermediate values of α are found, whereas for t-nitrobutane α has its lowest value. In cases where data are available for both the homogeneous and heterogeneous reaction (CB and DAB), it is seen that α increases in going from the homogeneous reaction to the heterogeneous one. This can be attributed to a corresponding decrease in ΔG^*_{is} relative to ΔG^*_{os}, or to an increase in donor-acceptor coupling. On the basis of the present results, the analyses of the heterogeneous DAB and phenothiazene data given earlier [15,17,27] are incorrect in that it was assumed that the coefficient α is one.

The kinetic data for those systems in which the parameter α can be considered unity within experimental error were reanalyzed on the basis of eq. (18) in order to determine the size-distance parameter R_p and the pre-exponential parameter, κK_p. These results together with the molecular radius estimated from crystallographic or density data are summarized in Table 4. The kinetic data for DMCB which fulfill the criteria for application of eq. (18) in both the homogeneous and heterogeneous reactions are also presented in Fig. 1. It is interesting that the estimates of R_p for this system are equal within experimental error. Thus, the slope of the plot for the homogeneous data is approximately twice that for the heterogeneous data. The parameter R_p which is equal to $R_h a / (R_h - a)$ in the case of homogeneous reactions, and $R_e a / (R_e - a)$ in the case of heterogeneous reactions is expected in general to be different in the two reaction modes. The fact that R_p is approximately independent of reaction mode in the case of DMCB suggests that imaging effects are important in the heterogeneous reaction. In previous analyses of solvent effects on heterogeneous electron transfer data [15-18], ΔG^*_{os} has been estimated assuming that $R_p = a$, that is assuming that imaging is not important ($R_e = \infty$). On the basis of the data summarized in Table 4, R_p is always greater than the reactant radius a, so that the assumption that $R_p = a$ can lead to serious over-estimation of ΔG^*_{os}. Estimation of R_p is not simple for polyatomic molecules under any circumstances. This aspect of the variation in ΔG^*_{os} with solvent has been discussed by Jaenicke and coworkers [7-9] who have demonstrated the importance of considering carefully molecular shape in estimating the size-distance parameter. This feature of electron transfer theory becomes more important with increase in the number of atoms in the reactant since the mutual orientation of the reactants in the transition state must be considered, electron transfer often being associated with a specific location in the molecule. Nevertheless, in spite of the fact that the τ_L solvent dependence plays a dominant role in determining the net solvent effect, the present results provide very strong confirmation of the Marcus model for ΔG^*_{os}.

It is also interesting to compare the values of the pre-exponential parameter, κK_p, with that predicted on the basis of the encounter pre-equilibrium model [25,30]. Assuming that $R_h = 2a$ and $\delta r = 60$ pm [30], κK_p for homogeneous adiabatic reactions varies between 0.16 and 0.45 $dm^3\ mol^{-1}$ for variation in the reactant radius between 0.3 and 0.5 nm (see eq. (6)). The value of κK_p obtained for TCQM, namely, 0.6 $dm^3\ mol^{-1}$ is slightly higher than expected on the basis of the parameters listed in Table 4, but is of the correct order of magnitude. In the case of DMCB, the estimate of κK_p is higher than expected by a factor of 30. This can be partially attributed to the poor quality of the fit which may lead to a low value of the size-distance parameter and thus a high value of κK_p. If one forces the size-distance parameter to be 0.96 nm ($R_p = 2a$), the estimate of κK_p drops to 1.3 $dm^3\ mol^{-1}$, a result which is closer to the range of values predicted by theory. In fact, Nielson et al [10] achieved agreement between experimental and theoretically predicted values of this parameter when it was assumed that $R_p = 1.3$ nm. In order to improve the quality of the fit, data are needed in more solvents with an improvement in the precision of the estimates of τ_L. The latter point is discussed in more detail below. In the case of the heterogeneous data, the experimental values of κK_p all fall below the predicted value of 60 pm for adiabatic reactions [30]. In analyzing these data, it has been customary in previous work [15-18] to assume that the size distance parameter R_p is equal to the molecular radius a, and to assess the solvent dependence using values of ΔG^*_{os} estimated accordingly (see eq. 3). In the case of the cobaltacene system for which the most data are available, the estimate of κK_p assuming $R_p =$ 0.37 nm is 380 pm, a result which is an order of magnitude higher than that predicted by theory. A fact that should be considered in assessing the heterogeneous results is that double layer effects have been ignored in analyzing the data for most systems [15-18]. Thus, the true or double layer corrected pre-exponential factor may be higher or lower than that given in Table 4 depending on whether the electrode's field accelerates or decelerates the reaction.

Kinetic data for which α can be assumed zero were reanalyzed according to eq. (17), the results being summarized in Table 5. The four systems which fulfill the criteria for application of eq. (17) are the homogeneous electron transfer reactions involving diaminobenzenes studied by Grampp and Jaenicke [7]. As reported earlier [7], the size-distance parameter for these systems is much larger than twice the molecular radius, that is, the value expected for spherical reactants at contact. This feature can be attributed to the non-spherical nature of the reactant and has been discussed in detail earlier [7]. What is more interesting here is the relative values of ΔG^*_{is} and ΔG^*_{os} and the reason why these systems exhibit little or no dependence of the pre-exponential factor on τ_L. On the basis of the size-distance parameters recorded and choosing an average value of the permittivity parameter γ (0.4), the average value of ΔG^*_{os} is approximately twice that of ΔG^*_{is}. Thus, the Ovchinnikova criterion [3,13] is not met for most of the solvents involved. In going from the homogeneous to the heterogeneous system, one finds an increase in the τ_L contribution to the solvent effect in the case of DAB. This cannot be attributed to an increase in ΔG^*_{os} with respect to ΔG^*_{is} unless there is a corresponding decrease in the size-distance parameter by a factor of two, or unless orientational requirements manifested in the respective values of ΔG^*_{os} only are very different for the electrode reaction with respect to the homogeneous one.

In assessing the above results one should keep in mind that the parameter τ_L, which accounts for the major portion of the solvent effect, is often imprecisely known and depends on the nature of the indifferent electrolyte [35]. Although the Debye relaxation time τ_D can be determined with reasonable precision, the infinite frequency dielectric constant ε_∞ has often been estimated on the basis of dielectric relaxation data obtained in too low a frequency range, long extrapolations to frequencies up to ~1 THz being required. As an example, we cite the data for propylene carbonate [41-44], an aprotic solvent with a high dielectric constant and long relaxation time. The available data which are summarized in Table 6 demonstrate clearly that the estimates of τ_L vary over an unacceptably wide range and that the major source of imprecision is the high frequency dielectric constant ε_∞. As

the Debye relaxation time decreases, the problem becomes worse because measurements at higher frequencies are required to determine ε_∞. In fact, for solvents with fast relaxation times such as acetonitrile, the values of ε_∞ are only estimates, no experimental values being available. The problem addressed here is apparent in the discussion of other experimental results, especially those related to time resolution studies of fluorescence phenomena in different solvents [45,46]. It is clear that more data for solvent relaxation processes are required in a higher frequency range both in the presence and absence of electrolytes before the questions raised here can be resolved. In the analyses presented here, when more than one estimate of τ_L is available from the literature the value chosen was that which resulted in the best fit of eq. (16) to the kinetic data (see Table I).

On examining the literature dealing with experimental data for solvent effects on electron transfer reactions [6-19], it is readily apparent that conclusions quite different than those reached here have been reported in many cases. This situation has arisen because it has been common practice to assume a certain solvent dependence for the free energy barrier in the rate constant and then examine the solvent dependence of the pre-exponential factor. We emphasize that the procedure described here allows one to separate the dependences on the permittivity parameter γ and the longitudinal relaxation time τ_L subject to the number and quality of the corresponding data, and thus reach statistically more sound conclusions regarding roles of these two parameters in determining the observed rate constant. For instance, Nielson et al. [10] concluded that kinetic data for DMCB in the homogeneous mode have a fractional dependence on τ_L ($0.7 > \alpha > 0.85$) whereas the present analysis shows that α is much closer to unity. This disagreement is almost certainly due to the fact that these authors assumed the dependence of the kinetic data on γ to obtain the dependence on τ_L. Since the dependence on γ makes up close to 40% of the total explained variation, their analysis is clearly subject to doubt.

In conclusion, the value of the present analysis is clearly dependent on the validity of eq. (12). We have already pointed out above that in some cases the parameter α may

depend on solvent nature for the range of solvents considered in a given analysis. In this case, our analysis gives a good indication of the relative importance of the two parameters in determining the solvent effect but the derived value of α must be considered an average value. There are other problems of a more subtle nature that could be considered, one of them being the fact that R_e is expected to change with solvent nature for heterogeneous reactions due to a corresponding variation in the distance of closest approach of the reactant to the electrode with solvent size [27]. However, the most important problem is the poor quality of the τ_L data for many of the solvents considered in current experimental studies. Further experimental work investigating solvent relaxation behaviour at high frequencies would do much to improve our understanding of the solvent's role in the kinetics of reactions in solution.

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Table 1. Solvent Parameters Relevant to Estimation of the Electron Transfer Rate Constant (Eq. 19)

Solvent	Longitudinal Relaxation Time[a] τ_L, ps	Permittivity Parameter[b] γ
Acetone (AC)	0.3	0.495
Acetonitrile (AN)	0.2	0.529
Benzonitrile (BN)	5.8	0.390
Chloroform (CF)	2.4	0.276
Dichloroethane (DCE)	1.6	0.384
Dichloromethane (DCM)	0.9	0.382
Dimethoxyethane (DMXE)	0.8	0.371
Dimethylacetamide (DMA)	1.5	0.459
Dimethylformamide (DMF)	1.1	0.463
Dimethylsulfoxide (DMSO)	2.1	0.437
Hexamethylphosphoramide (HMPA)	8.8	0.438
Nitrobenzene (NB)	5.3	0.387
Nitromethane (NM)	0.2	0.498
Propylene Carbonate (PC)	1.7	0.480
Pyridine (PY)	1.3	0.359
Tetrahydrofuran (THF)	1.7	0.388
Tetramethylurea (TMU)	6.0	0.433

[a] Defined in eq. (10).

[b] Defined in eq. (14).

Table 2. Analysis of the Dependence of Homogeneous Electron Transfer Rate Constants on Solvent Properties (Equaiton 19)

Reaction	Longitudinal Relaxation Time Coefficient α	Normalized Partial Regression Coefficients $\bar{\alpha}$	$\bar{g}$	Number of Solvents n	Regression Coefficient r
1. 1,4-diaminobenzene (0/+)[7]	0.1 ± 0.1	0.10	0.90	5	0.997
2. N,N-dimethyl-1, 4-diamino-benzene (0/+)[7]	0.1 ± 0.1	0.11	0.89	5	0.996
3. 2,3,5,6-tetramethyl-1,4-diaminobenzene (0/+)[7]	0.1 ± 0.1	0.10	0.90	5	0.995
4. N,N,N',N'-tetramethyl-1, 4-diaminobenzene (0/+)[7]	0.07 ± 0.03	0.11	0.89	6	0.999
5. tetracyanoquinodimethane (0/-)[8]	1.0 ± 0.2	0.62	0.38	5	0.946
6. cobaltacene (0/+)[10]	0.5 ± 0.2	0.50	0.50	11	0.785
	(0.7 ± 0.1	0.54	0.46	9	0.914)[a]
7. decamethylcobaltacene (0/+)[10]	0.8 ± 0.4	0.63	0.37	7	0.790
	(1.1 ± 0.3	0.58	0.42	6	0.944)[a]
8. ferrocene (0/+)[6]	0.6 ± 0.1	0.64	0.36	7	0.914

[a] Improved fits obtained by removing outlying points; see text for details.

Table 3. Analysis of the Dependence of Heterogeneous Electron Transfer Rate Constants on Solvent Properties (Equation 19)

Reaction	Longitudinal Relaxation Time Coefficient α	Normalized Partial Regression Coefficients $\bar{\alpha}$	$\bar{g}$	Number of Solvents n	Regression Coefficient r
1. cobaltacenium (+/0)[18]	1.0 ± 0.1	0.76	0.24	9	0.977
2. cyclooctatetraeniron tricarbonyl (0/-)[18]	1.2 ± 0.8	0.67	0.33	4	0.999
3. decamethylcobaltacenium (+/0)[16]	0.8 ± 0.9	0.78	0.22	4	0.979
4. bis(benzene)chromium (+/0)[16]	0.7 ± 0.6	0.90	0.10	5	0.992
5. phenothiazene (0/+)[15]	0.7 ± 0.1	0.71	0.29	7	0.972
6. 1,4-diaminobenzene (0/+)[17]	0.6 ± 0.1	0.96	0.04	7	0.965
7. t-nitrobutane (0/-)[19]	0.3 ± 0.3	0.35	0.65	4	0.853

Table 4. Kinetic Parameters for Adiabatic Electron Transfer Reactions for which $\Delta G^*_{is} << \Delta G^*_{os}$ (Equation 18).

Reactant	Molecular Radius[a] a, nm	Size-Distance Parameter R_p, nm	Inner Sphere Reorg. Energy ΔG^*_{is}, kJ mol^{-1}	Pre-Exponential Parameter[b] κK_p	Number of Solvents	Regression Coefficient
Homogeneous Reactions						
decamethylcobaltacene 0/+)[10]	0.48	0.65±0.15	1.84	13 ± 30	7	0.888
tetracyanoquinodimethane(0/-)[8]	0.44	1.7 ± 0.3	4.95	0.6±0.3	5	0.954
Heterogeneous Reactions						
cobaltacene (0/+)[16,18]	0.37	0.81±0.15	1.46	2 ± 2	9	0.895
decamethylcobaltacene (0/+)[16]	0.48	0.57±0.12	0.92	9 ± 11	4	0.959
cyclooctatetraeniron tricarbonyl (+/0)[18]	0.39	0.55 ± 0.09	-	-	4	0.975
bis(benzene)chromium (+/0)[16]	0.37	0.94 ± 0.20	1.05	1 ± 1	5	0.936

[a] Calculated from density or crystallographic data assuming that the volume per molecules is $4\pi a^3/3$.

[b] The units of K_p are dm^3 mol^{-1} for homogeneous reactions and pm for heterogeneous reactions.

Table 5. Kinetic Parameters for Electron Transfer Reactions Analyzed According to Equation 17.

Reactant	Molecular Radius[a] a, nm	Size-Distance Parameter R_p, nm	Inner Sphere Reorg. Energy[b] ΔG^*_{is}, kJ mol^{-1}	Pre-Exponential Parameter $10^{-11}\kappa K_p \nu_{is}$, dm^3 mol^{-1} s^{-1}	Number of Solvents	Regression Coefficient
Homogeneous Reactions						
1,4-diaminobenzene (0/+)[7]	0.30	1.64±0.11	3.55	1.2 ± 0.3	5	0.994
N,N-dimethyl-1,4-diamino-benzene (0/+)[7]	0.34	1.71 ± 0.11	3.40	1.9 ± 0.5	5	0.994
2,3,5,6-tetramethyl-1,4-diaminobenzene (0/+)[7]	0.36	1.85 ± 0.14	3.90	2.2 ± 0.6	5	0.992
N,N,N',N'-tetramethyl-1,4-diaminobenzene (0/+)[7]	0.36	1.98 ± 0.09	3.75	2.3 ± 0.3	6	0.996

[a] Calculated from density or crystallographic data assuming that the volume per molecule is $4\pi a^3/3$.

[b] Based on estimates made by Grampp and Jaenicke [7] and revised by Kapturkiewicz and Jaenicke [40].

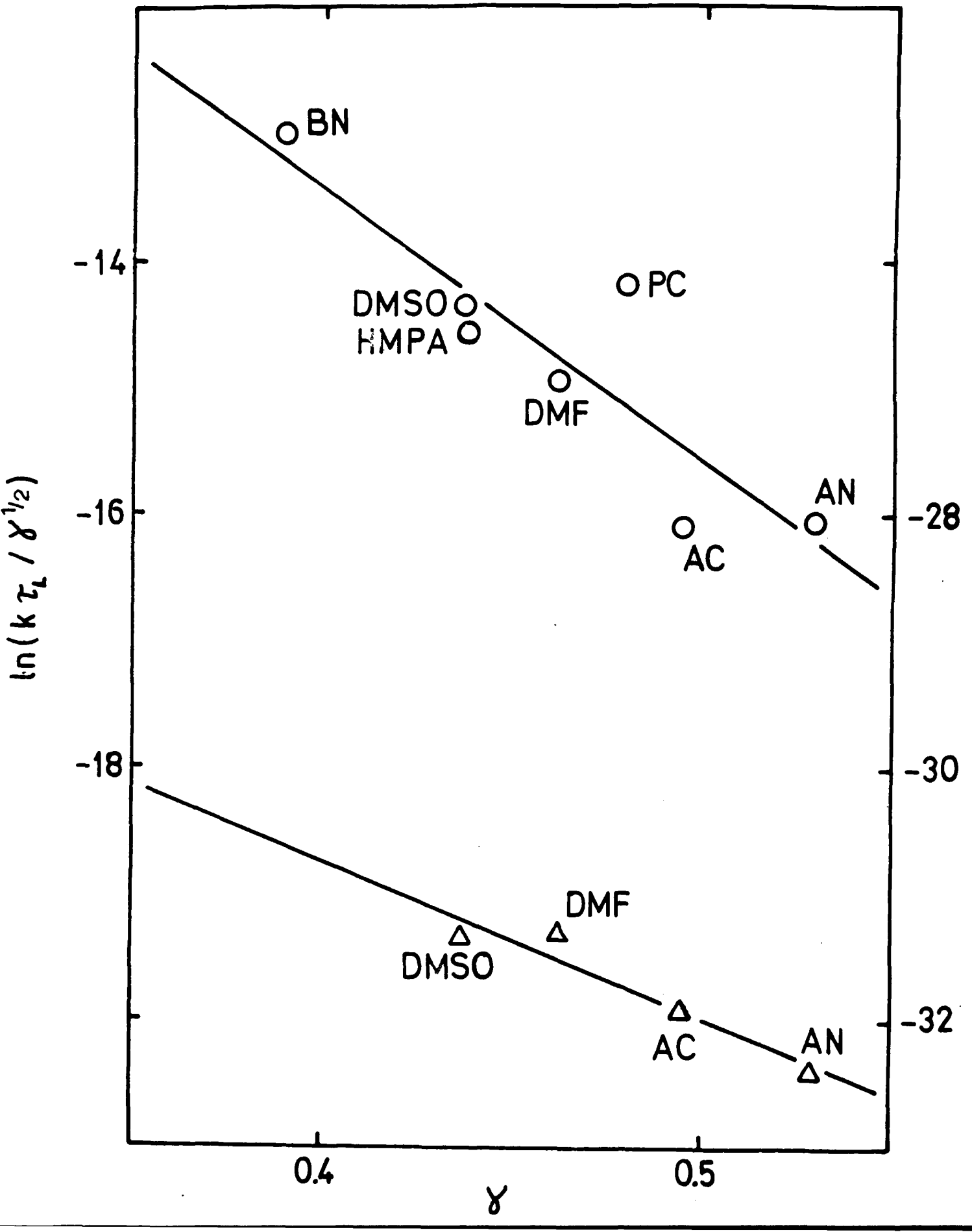
Table 6. Dielectric Relaxation Parameters for Propylene Carbonate at 25 °C

Static Dielectric Constant ε_s	High Frequency Dielectric Constant[a] ε_∞	Debye Relaxation Time[a] τ_D, ps	Longitudinal Relaxation Time τ_L, ps	Reference
64.9	2.6	43	1.7	41
64.0	5.5	39	3.4	42
64.9	12.5	44	8.5	43
64.7	6.2	39.4	3.8	44

[a] Parameters obtained by fitting dielectric relaxation data to the simple Debye model with a single relaxation time.[44]

Legends for Figures

Figure 1. Plot of the solvent corrected kinetic parameter ln ($k \tau_L/\gamma^{1/2}$) against the permittivity parameter γ using kinetic data for homogeneous electron transfer (O)[10] and heterogeneous electron transfer (Δ)[18] for the decamethylcobaltacene - decamethylcobaltacenium system. The left hand ordinate scale applies to the homogeneous data and the right hand scale, to the heterogeneous data.


BN
PC
DMSO
HMPA
DMF
AN
AC
DMF
DMSO
AC
AN
-14
-16
-18
-28
-30
-32
0.4
0.5
γ
ln(k τ_L / γ^1/2)