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A Comparison of Solvent Effects in the Kinetics of Simple Electron Transfer and Amalgam Formation Reactions

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A Comparison of Solvent Effects in the Kinetics of Simple Electron Transfer and Amalgam Formation Reactions*

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Summary

The ~~effect~~ effects of the solvent on the kinetic parameters of simple electron transfer and amalgam formation reactions are reviewed and compared. The parameters considered are the standard potential, the standard rate constant and the intrinsic transfer coefficient. The role of the solvent in double layer effects is also considered. Comparison of solvent effects on the standard rate constant reveals a major difference between the two reactions. This difference lends support to the conclusion that electron transfer is not involved in amalgam formation as the rate determining step. Instead, the rate determining step in amalgam formation involves movement of the reacting ion from one location in the double layer to another closer to the interface. The role of solvent dynamical processes in determining the rate constant is discussed with respect to the mass of the moving reactant and its interaction with the solvent environment.

Keywords: electrocatalysis, thermodynamics, transfer coefficients, (KR)

Introduction

The role of the solvent in simple heterogeneous electron transfer processes has been investigated in some detail recently[1-6], and the influence of solvent dynamical properties on the rate constant[7-11] clearly demonstrated.[4,5,12] The important feature of recent theoretical work[7-11] has been the recognition that the value of the pre-exponential factor in the rate constant depends on the dynamics of solvent relaxation processes which determine the frequency with which the activated complex is formed. When charge is displaced in a reaction in a condensed phase, the surrounding dipoles respond in a time dependent way to the motion. The importance of solvent dynamics depends on the mass of the moving charge and the forces binding the charge to the surrounding dipoles.[9]

Amalgam formation reactions have been traditionally regarded as processes in which the rate controlling step is electron transfer.[13] This implies that intermediate species, such as ions of lower charge or atoms which are normally unstable, are formed in the double layer near the electrode. An alternative mechanism of amalgam formation is one in which ion movement through the double layer is the rate controlling step.[14] Obviously, the solvent plays in important role in ion transfer, especially when the metal ion is surrounded by solvent molecules in its primary solvation sheath. One step in the ion transfer mechanism involves partial replacement of the solvent molecules in the intermediate atomosphere of the metal ion with mercury atoms. The energetics associated with such a step are obviously very different from those associated with electron transfer. In the latter process, the heavy particle to which or from which the electron is transferred remains relatively immobile, and the activation process involves solvent reorganization around the heavy particle.[15] On the other hand, in an ion movement process, the ligands surrounding the ion are either moved through space, or displaced and replaced by new ligands. Thus, solvent effects for electron and ion transfer processes should be markedly different.

The purpose of the present paper is to examine and compare solvent effects for electron transfer and amalgam formation reactions with respect to all solvent dependent parameters. These include thermodynamic parameters such as the standard potential of the reaction, and kinetic parameters such as the standard rate constant and apparent transfer coefficient. As far as the solvent is concerned, two properties that are of interest are its permittivity, both static and in the limit of very high frequencies. The latter quantity is normally considered to be the square of the refractive index measured using the sodium D line. Another property, whose importance has been recognized in recent theoretical work[7-11], is the Debye relaxation time. As far as solvating ability at the molecular level is concerned, empirical measures of the solvent's ability to act as an electron pair donor or acceptor, namely, the donor number and acceptor number are useful in assessing variation in thermodynamic quantities with the nature of the solvent. These properties for some aprotic solvents commonly used in electrochemistry are summarized in Table I. Although solvent effects on kinetic parameters also have been measured in some protic solvents, there is clear evidence that solvent effects in these systems are different than in aprotic systems[4-6], probably as a result of the more complex dielectric relaxation behaviour observed due to hydrogen bonding.[11] For this reason, results in protic solvents are not considered in this paper.

The Kinetic Parameters

We consider the general reaction

$$A + ne \rightarrow B \qquad (1)$$

where the reactant A is in the double layer and the product B is either in the double layer or dissolved in the mercury phase. In the case of simple electron transfer processes, the number of electrons, n, is either +1 corresponding to reduction or -1 corresponding to oxidation. In the present paper, only electron transfer reactions involving molecules are considered so that the product B is either an anion radical or a cation radical. Moreover, since the reaction is simple, the rate determining step (r.d.s.) is also the overall reaction. In the case of amalgam formation, the mechanism of the reaction involves several steps, and the nature of the r.d.s. can change with potential.[14] In general, one may distinguish four possible elementary steps. These are discussed with respect to the case of the reduction of sodium ion at mercury in a dimethylformamide (DMF) solution containing tetraethylammonium perchlorate (TEAP) as background electrolyte (see Fig. 1). One possible elementary step is electron transfer in which an electron moves from the mercury phase to the metal ion in the vicinity of the electrode. The metal ion, which may be the original reactant or an intermediate (e.g. Zn^+ in the case of Zn^{++}), is assumed to be totally surrounded by solvent molecules, and not to be in intimate contact with the electrode. In the present example, electron transfer can occur when the Na^+ ion is at location 'c' just outside the outer Helmholtz plane (o.H.p.) or at location 'b' in the inner layer. The second possible step is ion transfer in which the original reactant or an intermediate moves from one location in the double layer to another which is closer to the electrode. The ion experiences a change in electrostatic potential and may lose some of its solvation sheath in this step, but it does not come in contact with the mercury phase. Obviously, this step corresponds to movement from location 'c' to location 'b'. Although no electrons are transferred in this step, it occurs in the field of the electrode and involves the movement of charge. As a result, its kinetics are potential dependent. A third possible step is adsorption in which the ion moves from location 'b' to location 'a', that is, from a site in the inner layer where it is completely surrounded by solvent molecules to a site at the interface where it is partially solvated by solvent molecules and partially solvated by mercury atoms. This step is assumed to be accompanied by partial charge transfer so that the net charge on the adsorbed species is intermediate between that on the original ion and zero. Finally, there is a metal incorporation step in which the adsorbed metal species moves from the adsorption site to the mercury phase.

When the potential dependence of each of the elementary steps is considered in detail[14], it can be shown that the form of the kinetic equation is exactly the same for each step. This follows from the fact that they each involve the movement of charge in an electrical field. However, the interpretation of the kinetic parameters and their dependence on the nature of the solvent will vary greatly depending on the nature of the elementary step. When one of these steps is rate determining, then the familiar kinetic equation for a heterogeneous reduction process may be used. In the case that specific adsorption of other ions or solute molecules is absent, the logarithm of the forward rate constant is given by

$$\ln k_f = \ln k_s + (\alpha_a n - z_A) f\phi^d - \alpha_a n f (\phi^m - \phi_r^m) \tag{2}$$

where k_s is the standard rate constant, ϕ^m, the electrode potential, ϕ_r^m, the standard electrode potential, or more often, the formal electrode potential, ϕ^d, the potential drop across the diffuse layer as estimated by the Gouy-Chapman theory, α_a, the apparent transfer coefficient, z_A, the charge on the reactant and $f = F/RT$. The relationship between the apparent transfer coefficient, α_a, and the intrinsic or true transfer coefficient, α, depends on the nature of the r.d.s. The two quantities are equal when the reactant is located on the outer Helmholtz plane during the r.d.s. and only electrons are transferred. Otherwise, the apparent transfer coefficient also depends on the charge on the reactant and its location in the double layer during the r.d.s. In general, for amalgam formation reactions, the value of α_a increases when the rate determining step is located closer to the electrode.[14] This conclusion simply reflects the fact that the changes in electrostatic potential in the double layer become more pronounced with changes in the electrode potential as the reaction site moves closer to the interface.

It is obvious that the formal potential, the standard rate constant, and the potential drop across the diffuse layer depend on the nature of the solvent. The dependence of the standard rate constant on solvent nature can only be properly analyzed when the kinetic data are corrected for double layer effects. For amalgam formation reactions with adsorption as the r.d.s, the intrinsic transfer coefficient can also depend on the nature of the solvent as will be discussed below. In the case of the standard rate constant, the solvent is recognized to influence both the pre-exponential factor, Z, and the standard free energy of activation, $\Delta G_s^{\ddagger}$, as defined by the following equation

$$\ln k_s = \ln Z - \Delta G_s^{\ddagger}/RT \qquad (3)$$

The dynamical properties of the reaction medium influence the frequency with which the activated complex is formed and, thus, the preexponential factor. On the other hand, the manner in which $\Delta G_s^{\ddagger}$ depends on the solvent changes with the nature of the r.d.s.

In the following sections of this paper, the nature of the solvent dependence of the various terms in equation (2) are discussed and experimental results compared for electron transfer and amalgam formation reactions. As one would expect, these reactions should differ most significantly with respect to the influence of the solvent on the standard rate constant and transfer coefficient. Data available in the literature are considered, and the role of electron transfer in amalgam formation reactions assessed.

The Formal Potential

The standard potential is a thermodynamic quantity whose value depends on the solvation of the reactants and products of the electrode reaction (reaction (1)) in the phase in which they are located. However, in order to compare standard potentials in various solvents, one must have a solvent independent reference potential. One system that has been widely used in this regard is the ferrocene/ferrocenium ion couple.[16,17] It is assumed that the cyclopentadiene rings surrounding the iron in this system effectively isolate the iron atom or ion from the solvent environment so that the standard potential on an absolute scale is independent of solvent nature. Another organometallic system which has been used in this regard is bis(biphenyl)chromium(I)/(O).[16,18] If one uses such an extrathermodynamic assumption and corrects the observed standard potentials for the reaction in question to a solvent independent reference, one can consider solvent effects on the thermodynamic parameters for the given half-reaction.

A useful way of describing solvent effects on thermodynamic quantities is in terms of the Lewis acid and base properties of the solvent.[19,20] Accordingly, the dependence of quantity Q on these properties is written

$$Q = Q_o + a\,AN + b\,DN \qquad (4)$$

where AN is the acceptor number of the solvent, a measure of its Lewis acidity[21], DN, is the donor number, a measure of its Lewis basicity[22], and a and b, measure the dependence of the given quantity on solvent acidity and basicity, respectively. The acceptor number and donor number are empirical measures of solvent acidity and basicity, and there is an increasing body of evidence that they provide useful measures of the solvating ability of solvents for ions and dipoles.[16,19,20,23] Values for a variety of non-aqueous solvents are summarized in Table I.

The parameter reported in electrode kinetic experiments is normally the formal potential, ϕ_r^m, not the standard potential, ϕ_s^m. The relationship between these quantities for reaction (1) is

$$\phi_r^m = \phi_s^m - \frac{RT}{nF} \ln \frac{\gamma_B}{\gamma_A} \qquad (5)$$

where γ_A is the activity coefficient of A at unit concentration and γ_B, that for B. Although both activity coefficients depend on the nature of the solvent especially when one or both of A and B are ions, this dependence is minor compared to that of the standard potential itself. This point is considered further below.

In the case of a simple electron transfer reaction involving reduction of a molecule to form an anion radical,

$$A + e \rightarrow A^{\overline{\cdot}} \qquad (6)$$

the properties of the solvent are most important with respect to solvation of the anion, that is, with respect to its ability to act as a Lewis acid. Then, to a good approximation, the variation in the formal potential with solvent can be expressed as

$$\phi_r^m = \phi_{ro}^m + a\,AN \qquad (7)$$

where ϕ_{ro}^m is the formal potential in a solvent with zero acceptor number, and a measures the degree to which the formal potential changes with increase in AN. Formal potential data for the reduction of phenazine at mercury in eight different aprotic solvents measured with respect to the standard potential of the ferrocene/ferrocenium ion couple in the same solvent[24] are plotted against the solvent's acceptor number in Fig. 2. As discussed earlier by Paduszek and Kalinowski[24], an excellent correlation between the thermodynamic data and the Lewis acidity parameter is obtained ($r = 0.993$). The fact that ϕ_r^m becomes more positive with increase in AN confirms that the product anion radical is correspondingly more strongly solvated. At the same time, the standard free energy change becomes more negative, and ϕ^m shifts in the positive direction since the reaction involves reduction. Similar results were obtained by Kapturkiewicz and Opallo[2] for the reduction of nitromesitylene in different non-aqueous solvents in the presence of electrolytes which did not ion pair with the resulting anion radical (tetraethylammonium and tetrabutylammonium perchlorates).

In the case of a simple electron transfer reaction involving oxidation of a molecule to form a cation radical,

$$A \rightarrow A^{+\bullet} + e \qquad (8)$$

the properties of the solvent are chiefly manifested through solvation of the cation, that is, with respect to its ability to act as a Lewis base. It follows that the change in formal potential with solvent is approximately given by the expression

$$\phi_r^m = \phi_{ro}^m + b\,DN \qquad (9)$$

where ϕ_{ro}^m is the formal potential in a solvent with zero donor number, and b, the degree to which the formal potential changes with increase in DN. Formal potential data for the oxidation of 1,4-diaminobenzene at platinum in eight different aprotic solvents measured with respect to the formal potential of the ferrocene/ferrocenium ion couple in the same solvent with $NaClO_4$ as background electrolyte[5] are shown as a function of the solvent's donor number in Fig. 3. The correlation obtained in this case is quite good ($r = 0.935$), the formal potential shifting in the negative direction with increase in solvent donicity. Similar results were obtained by Paduszek and Kalinowski[24] for the oxidation of phenothiazine at platinum in nine non-aqueous solvents. The negative correlation obtained in this case also confirms that the product cation radical is more strongly solvated in solvents of higher donor number. As the DN increases, the standard free energy change becomes more negative but ϕ_r^m shifts in the negative direction because an oxidation process is involved.

The final example considered here is the case of amalgam formation reactions for which the overall reaction is

$$M^{+n} + ne \rightleftharpoons M(Hg) \qquad (10)$$

Since the present discussion is limited to the case that the reactant is solvated by solvent molecules only, the reactant is always a cation and the solvent effect on the formal potential is expressed only in terms of the solvent's ability as a Lewis base to solvate the reactant. Thus, to a good approximation, the dependence of the standard potential on solvent is given by eq. (9). Gritzner[18] has demonstrated that this relationship is valid for half-wave potential data for the reduction of alkali metal cations and other cations including Tl^+, Cu^+, Ag^+, Zn^{++}, Cd^{++}, Cu^{++} and Pb^{++} using the bis(biphenyl)chromium(I)/(O) reference. It should be remembered that the half-wave potential depends on the diffusion coefficients of M^{+n} and M in their respective phases, and is related to the formal potential for a reversible polarographic wave by the equation

$$\phi^m_{1/2} = \phi^m_r + \frac{RT}{2nF} \ln \frac{D_M}{D_{M^+}} \qquad (11)$$

Obviously, the diffusion coefficient, D_{M^+}, depends on the nature of the solvent so that half-wave potential data contain solvent dependent contributions from the diffusion coefficient and activity coefficient of M^{+n} as well as the main contribution from the solvent dependence of the standard free energy of reaction (10). The fact that good correlations were obtained for most systems by Gritzner[18] suggests that the contribution to the solvent effect from the change in the standard free energy predominates. The correlation obtained with data for the reduction of Cd^{++} in 13 aprotic solvents[25] in which the reduction wave is reversible or nearly reversible[27] is shown in Fig. 4. It is apparent that a very good correlation is obtained over a wide range in DN ($r = 0.960$) and that a significant variation in $\phi_{1/2}^{m}$ with solvent donicity is observed (~ 800 mV). As the donor number of the solvent increases, the reactant is stabilized and the standard free energy change for reaction (10) becomes more positive; since the reaction involves reduction, this results in the standard potential shifting in the negative direction.

As pointed out above, the formal potential contains an additional solvent dependence with respect to that of the standard potential through the dependence of the activity coefficients of the reactant and/or product on the nature of the solvent (eq. (5)). The main contribution to any solvent effect is from ionic components of the reaction whose activity coefficients depend on the ionic strength of the electrolyte solution in which they are located and the dielectric constant of the solvent. The dielectric constant for most of the solvents considered falls in the range from 25 to 45 so that the change in the logarithm of the activity coefficient estimated by the Debye-Huckel theory in solutions of constant ionic strength is not large. Some solvents such as tetrahydrofuran have significantly lower dielectric constants and form electrolyte solutions with a large fraction of ion pairs so that the difference between ϕ_{r}^{m} and ϕ_{s}^{m} is expected to be different than that for most other solvents. However, when one considers the data which deviate most from the correlations presented in Figs. 2-4, no simple explanation for the deviations is apparent. Obviously, the above correlations should be reconsidered when activity coefficient data are available. In the meanwhile, the simple model presented by Krygowski and Fawcett[19,20] provides a very good account of the experimental trends observed.

Finally, it should be noted that solvent effects on the thermodynamic parameters of electron transfer reactions have also been investigated for the entropy change ΔS^{o} accompanying anion radical formation (reaction (6)).[55,56] ΔS^{o} was estimated by measuring the temperature dependence of the half-wave potential in a non-isothermal cell. In the case of reduction of p-semiquinones[55] and p-dicyanobenzene[56], excellent correlations were obtained between ΔS^{o} and the acceptor number. In the case of the reduction of nitromesitylene, contributions to the solvent effect from both solvent basicity and acidity were found (eq. (4)). These results provide further evidence that the effects of solvation on thermodynamic properties can be accounted for to a good approximation using the empirical measures of solvent donor and acceptor properties provided by DN and AN.

The Double Layer Effect

The effect of the double layer on the kinetic parameters is traditionally assessed by assuming that the reaction takes place on the outer Helmholtz plane (o.H.p.) and estimating the potential on this plane, ϕ^d, using the Gouy-Chapman theory. Accordingly, ϕ^d is given by

$$\phi^d = \frac{2RT}{F} \ln \left[\frac{\sigma}{2A} + \left(\frac{\sigma^2}{4A^2} + 1 \right)^{\frac{1}{2}} \right] \tag{12}$$

where σ is the charge density on the electrode, and A is a solvent dependent parameter equal to $(2RT\varepsilon\varepsilon_0 c_s)^{1/2}$, ε_s being the static dielectric constant of the solvent, ε_o, the permittivity of free space, and c_s, the electrolyte concentration for a 1-1 electrolyte. It follows that ϕ^d depends on the dielectric constant of the solvent at constant electrolyte concentration and electrode charge density, decreasing with increase in solvent permittivity. Values of the parameter A estimated for $c_s = 0.1$ M at 25° C are given in Table II for solvents with a wide range of permittivity. Also listed are values of ϕ^d at an electrode charge density of $-10\ \mu C\ cm^{-2}$. This parameter changes by ~50 mV when the solvent is changed from acetone with $\varepsilon_s = 20.6$ to N-methyl formamide with $\varepsilon_s = 182$. In the range of dielectric constants typical of commonly used aprotic solvents, the change is somewhat less, on the order of ~30 mV. Also given in this table is the minimum accelerating factor for a typical electron transfer reaction involving formation of an anion radical from a molecule, and having a transfer coefficient of 0.5. This quantity varies by a factor of 2.7 over the given range and demonstrates that double layer effects must be considered if a precise analysis of solvent effects is to be made.

The above analysis oversimplifies the real situation by assuming that the charge density on the electrode is constant. In fact the electrode charge density at the standard potential for a given reaction varies with the solvent due to a corresponding variation in the potential of zero charge (p.z.c.)[28], and in the value of the capacity of the electrode/solution interface.[29] Values of the p.z.c. for nine non-aqueous solvents on the solvent independent ferrocene / ferrocenium ion scale are given in Table III. For the systems considered, this potential varies by ~130 mV. The variation in electrode charge density with electrode potential due to the corresponding change in double layer capacity also depends on the solvent and the base electrolyte. It follows that double layer capacitance data should be collected together with kinetic data so that corrections for double layer effects can be made.

It must be remembered that the double layer corrections have been traditionally described for electron transfer reactions in which the reactant and product are located on the o.H.p. In general, the location of the reaction site is not the same as that of the o.H.p. because of differences in the size of the reactant and the predominant counter ions which define the location of the o.H.p.[32] Under conditions where ionic specific adsorption is absent, the lack of coincidence of the reaction plane and o.H.p. leads to differences between the apparent transfer coefficient α_a and the true transfer coefficient α; the relationship between these quantities is

$$\alpha_a = \alpha + \lambda (z_A - \alpha) \tag{13}$$

where λ is a positive number for reaction sites in the inner layer and is equal to the ratio of the integral capacity of the inner layer to that between the reaction plane and o.H.p.[32] In the case of amalgam formation reactions, double layer effects also result in differences between the apparent transfer coefficient and the intrinsic quantity. When one compares these effects for elementary steps not involving electron transfer, one concludes that α_a increases for constant α as the location of the reaction site for the r.d.s. moves closer to the electrode.[14] Since one does not know where the reaction site is located with respect to the interface on the basis of the kinetic data alone, this subject is not pursued further here.

It is clear from the above discussion that correction of the kinetic data for the potential drop across the diffuse layer represents only a first order correction for double layer effects that should always be performed. However, in several recent studies of solvent effects in electron transfer reactions, double layer corrections have not been made[4-6] In the case of a study of the electrooxidation of 1,4-diaminobenzene at platinum[5], it was argued that since the reaction occurs close to the p.z.c., double layer effects are negligible. Although it may be true that the value of ϕ^d is small, the value of $\partial\phi^d / \partial\phi^m$ is largest at the p.z.c. Thus, failure to correct for double layer effects would lead to large errors in the apparent transfer coefficient, α_a. In the case of kinetic data for the electrooxidation of phenothiazine[4] and the electroreduction of the cobaltacenium cation[6], it was observed that the rate constant was independent of background electrolyte concentration. Although this is a surprising result, it does not warrant the conclusion that double layer effects are absent. Instead, it suggests that they are more complex than those observed in the simple cases which have been well documented in the literature.[33]

In conclusion, double layer corrections should always be made within the context of the Frumkin model before heterogeneous kinetic data are examined for solvent effects. Although it is recognized that these corrections are only approximate, their application removes a large fraction of the solvent effect due to the double layer from the kinetic parameters.

The Standard Rate Constant

As pointed out above, the standard rate constant for charge transfer processes depends on the nature of the solvent both with respect to the pre-exponential factor, Z, and the standard free energy of activation, $\Delta G_s^{\ddagger}$. In the case of Z, recent theoretical work[7-11] has discussed the fact that the frequencty with which the activation barrier is crossed depends on the rate of solvent dielectric relaxation. When charge moves in a reaction, the surrounding solvent dipoles respond in a time dependent way. As discussed by van der Zwan and Hynes[9], one may consider two extremes with respect to this process. At one extreme the charge moves so rapidly that the solvent dipoles are virtually frozen during the movement. At the other extreme, the charge moves so slowly that the solvation sheath around the reactant maintains an equilibrium configuration during the reaction. For cases in which the solvent forces are strong so that a reactive passage is controlled by slow solvent response, van der Zwan and Hynes[9] have shown that Z is proportional to τ_L^{-1}, where τ_L is the longitudinal or constant charge relaxation time for the solvent.[34] The condition to be met for strong solvent forces is that the square of the electrostatic solvent frequency, ω_s^2, be greater than the square of the chemical barrier frequency, ω_b^2. The electrostatic solvent frequency which governs short time displacement in a fixed reaction field is given by the following equation for solvents with dielectric constants greater than 20:

$$\omega_s = (z_i^2 \; e^2 / 4 \, \pi^2 \, \varepsilon_0 \, m \, \rho_o^3)^{1/2} \qquad (14)$$

Here, z_i is the valence of the charged species, e, the electronic charge, m, the mass of the species, and ρ_o, the radius of an infinite cylindrical cavity in the dielectric medium defining the charge transfer reaction coordinate. Assuming that the radius of the cavity is 0.1 nm, the value of ω_s for a proton is 2×10^{14} s^{-1}. For heavier charged particles such as a Li^+ ion or a Na^+ ion, it drops to 8.0×10^{13} s^{-1} and 4.4×10^{13} s^{-1}, respectively. Obviously, the electrostatic solvent frequency associated with electron transfer is at least an order of magnitude greater than that for proton transfer. Considering that chemical barrier frequencies are typically in the range 10^{12} to 10^{14} s^{-1}, it is clear that solvent dynamical effects are important in electron and proton transfer reactions. These effects become less important as the mass of the moving particle increases, and would only be observed for reactions with low chemical barriers. The relaxation time, τ_L, whose physical significance has been discussed by Friedman[34], is given by

$$\tau_L = \varepsilon_\infty \tau_D / \varepsilon_s \qquad (15)$$

where τ_D is the usual Debye relaxation time and ε_∞, the high frequency dielectric constant. The quantity ε_∞ has been interpreted by some authors as the dielectric constant observed at infrared or microwave frequencies, ε_{ir}, and by others as the optical dielectric constant, ε_{op} that is, the square of the refractive index normally cited for the sodium D line. The quantity ε_{ir} is always larger than ε_{op} but often not available precisely from data published in the literature because it was estimated by extrapolation of dielectric relaxation data obtained in an insufficiently wide frequency range. Differences in interpretation of ε_∞ have been discussed in the literature with respect to the alcohols[11,35] which have complex dielectric relaxation spectra. However, in the present discussion it is assumed that $\varepsilon_\infty = \varepsilon_{ir}$, in keeping with previous analyses of solvent effects on electron transfer reactions.[2-6]

According to the encounter preequilibirum model[36-38], the pre-exponential factor for an electron transfer reaction may be written

$$Z = \kappa K_p \nu_n \qquad (16)$$

where κ is the electronic transmission coefficient, K_p, the equilibrium constant for precursor complex formation, and ν_n, the nuclear frequency factor. Then, the standard rate constant corrected for double layer effects is given by

$$k_s = \kappa K_p \nu_n \exp(-\Delta G^* / RT) \qquad (17)$$

where ΔG^* is the reorganizational free energy of activation for electron transfer. The latter quantity is made up of an inner sphere contribution, ΔG^{*}_{is}, which may be calculated from the vibrational force constants for the reactant and the coordinate changes accompanying electron transfer[39,40], and an outer sphere contribution, ΔG^{*}_{os}, related to the work done to reorganize the solvent in the environment of the reactant. For systems in which $\Delta G^{*}_{os} >> \Delta G^{*}_{is}$, the nuclear frequency factor is described by the overdamped solvent relaxation model and is given by[7,10]

$$\nu_n = \frac{1}{\tau_L}\left(\frac{\Delta G^{*}_{os}}{4\pi RT}\right)^{1/2} \tag{18}$$

Finally, the Marcus expression relating ΔG^{*}_{os} to the dielectric properties of the solvent is

$$\Delta G^{*}_{os} = \frac{N_o e^2}{32\pi\,\varepsilon_o}\left[\frac{1}{r} - \frac{1}{R}\right]\left[\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right] \tag{19}$$

where N_o is Avogadro's number, r, the radius of the reactant represented as a sphere, and R, the distance of the charge center of the reactant from its image in the electrode. Combining eqs. (17) - (19), one obtains the expression

$$k_s = \frac{\kappa K_p}{\tau_L}\left[\frac{g\gamma}{4\pi}\right]^{1/2} \exp(-\Delta G^{*}_{is}/RT)\ \exp(-g\gamma) \tag{20}$$

where
$$\gamma = \frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s} \tag{21}$$

and
$$g = \frac{N_o e^2}{32\pi\,\varepsilon_o RT}\left[\frac{1}{r} - \frac{1}{R}\right] \tag{22}$$

From eq. (20), it is clear that the pre-exponential factor depends on the solvent through the permittivity parameter, γ, and relaxation time, τ_L, whereas the exponential term depends only on γ. Rearranging eq. (20) so that the standard rate constant is corrected for the solvent dependent terms in the pre-exponential factor, one may write

$$\ln \left[\frac{k_s \tau_L}{\gamma^{1/2}}\right] = \ln \left[\kappa K_p \left(\frac{g}{4\pi}\right)^{\frac{1}{2}}\right] - \frac{\Delta G^*_{is}}{RT} - g\gamma \tag{23}$$

It follows that a plot of $\ln \; (k_s \tau_L / \gamma^{1/2})$ against γ should be linear with a slope of -g. Furthermore, if ΔG^*_{is} is known one may estimate the product κK_p from the intercept. An analysis of kinetic data for heterogeneous electron transfer on the basis of eq. (23) permits one to determine the distance parameter $rR / (R-r)$ and the preencounter equilibrium parameter κK_p, which are important in assessing the location of the reactant in the double layer and reaction adiabaticity, respectively.

Values of the standard rate constant obtained by Opallo[5] for the electrooxidation of 1,4-diaminobenzene (DAB) in six different aprotic solvents are listed in Table IV in order of decreasing speed. Only those aprotic solvents for which τ_L values can be calculated from data in the literature, and which have static dielectric constants in the intermediate range are considered. With regard to the later point, it should be noted the solvents with very low dielectric constants such as tetrahydrofuran and dioxane have dielectric relaxation parameters which depend on the nature and concentration of the dissolved electrolyte.[41] From the data presented in Table IV, it is readily apparent that the standard rate constant decreases with increase in τ_L but that there is no correlation betwen k_s and the donor number of the solvent which describes solvation of the product cation radical. In fact, Opallo[5] showed a linear correlation between log k_s and log τ_L. Such a correlation ignores the solvent dependence of ΔG^* but demonstrates that the solvent dependence through τ_L dominates. It should also be noted the standard rate constant decreases by approximately a factor of ten when the solvent is changed from a "fast" one such as acetonitrile to a "slow" one such as hexamethylphosphoramide. A plot of the solvent corrected kinetic parameter $\ln (k_s \tau_L / \gamma^{1/2})$ against the permittivity parameter γ is shown in Fig. 5, a good linear correlation with a negative slope being obtained $(r = 0.88)$.[42] A similar plot with data for the cobaltacenium / cobaltacene (COB) system studied by McManis et al.[6] is shown in Fig. 6. In both cases, the magnitude of the slope yields very reasonable values of the distance parameter $rR/(R-r)$, namely, 0.60 ± 0.16 nm for DAB and 0.8 ± 0.3 nm for COB. Previous workers who analyzed these data assumed $R = \infty$ and set the distance parameter equal to the reactant radius, r, namely 0.34 nm in the case of DAB[5] and 0.38 nm in the case of COB.[6] Thus, on the basis of the present analysis, previous estimates of ΔG^*_{os} for these reactions are high by a factor of two. In fact, if one calculates R on the basis of previous estimates of r, which are certainly reasonable, it is apparent that R is close to 0.75 nm on the basis of the present analysis. The assumption that R is infinite is precarious theoretically, since the electronic transmission coefficient decreases exponentially with increase in R, and the reaction can no longer be considered adiabatic.

In order to estimate the parameter κK_p from the intercept of the plots shown in Fig. 5 and 6, one must have an estimate of ΔG^*_{is}. In the case of DAB, Grampp and Jaenicke[43] calculated ΔG^*_{is} to be 0.9 kJ mol^{-1}; accordingly, the estimate of κK_p on the basis of eq. (23) is 0.5 ± 0.8 pm. While the error in the estimate is large, the estimate of κK_p is two orders of magnitude smaller than the value of 60 pm proposed by Hupp and Weaver.[44] For the cobaltacenium system[6], where ΔG^*_{is} calculated to be 1.0 kJ mol^{-1}, the estimate of κK_p is 3 ± 5 pm. While larger than that for the DAB system, this result also suggests that previous estimates of κK_p are too high.

The present analysis demonstrates clearly that the description of solvent effects on k_s for simple electron transfer reactions is correct for cases in which the inner sphere contribution of the reorganizational free energy of activation is considerably less than the outer sphere contribution. Moreover, this analysis makes it clear for the first time that the

Marcus expression for ΔG^*_{os} is valid for heterogeneous electron transfer. There are some simplifying assumptions associated with the analysis used here, the chief one being that R is solvent independent. These assumptions have been discussed elsewhere.[12]

In view of the success experienced in understanding solvent effects on the standard rate constant for simple electron transfer reactions, it is interesting to examine and compare solvent effects on the same quantity for amalgam formation reactions. Such a comparison should permit one to determine whether electron transfer is the r.d.s. in the mechanism of the latter process. Values of k_s for the reduction of Li^+ in six aprotic solvents are presented in Table V. It is immediately apparent that the change in k_s when the solvent is changed from acetonitrile to hexamethylphosphoramide is a factor of 10^6, that is, much greater than in the case of a simple electron transfer reaction. These results suggest that the kinetic parameters of the r.d.s are more characteristic of those for charge transfer reactions involving heavier particles.[45] Similar results are obtained for the electroreduction of Na^+ in four solvents. However, in this case, the corresponding decrease in k_s from the "fast" solvent to the "slow" one is the order of 20. This observation undoubtedly reflects the fact that Na^+ is more weakly solvated than Li^+ because of its larger radius. If one ignores the data for propylene carbonate in the case of Li^+, it is clear that the standard rate constants for both reactants decrease with increase in τ_L and DN. Considering the fact that Li^+ is a quite light ion which interacts strongly with the solvent, it is reasonable to expect that solvent dynamical effects are important for the r.d.s. in this reaction. It was shown previously[46,47] that ln k_s for these reactions was linearly related to the free energy of solvation of the reactant, or to its donor number in a given solvent. It is now interesting to see whether such a correlation is maintained if one corrects for solvent dynamical effects in the pre-exponential factor. A plot of $\ln(k_s\tau_L)$ against DN for the Li^+ data is shown in Fig. 7, an excellent correlation being obtained ($r = 0.97$). In fact, inclusion of the τ_L correction results in values of $k_s\,\tau_L$ which decrease smoothly with DN, the problem with the relative positions of tetrahydrofuran and propylene carbonate in the table being resolved. The equation of the line shown in Fig. 7 is

$$\ln(k_s \tau_L) = -29.34 - 0.40 \text{ DN} \qquad (24)$$

As one might expect, an excellent correlation holds between the free energy of transfer of Li^+ ion from water to an aprotic solvent[16] and the DN, the corresponding equation being

$$\Delta G_t^o / RT = 25.5 - 1.08 \text{ DN} \qquad (25)$$

where ΔG_t^o is the free energy of transfer. This equation expresses the expected result that the free energy of solvation of the Li^+ becomes more negative as the donicity of the solvent increases. Combining eqs. (24) and (25), one may write the following relationship between the standard free energy of activation $\Delta G_s^\ddagger$ for Li^+ reduction and the free energy of solvation of the Li^+ ion reactant, ΔG_s^o:

$$\Delta G_s^\ddagger = \text{constant} + 0.37 \; \Delta G_s^o \qquad (26)$$

Thus, one finds a Bronsted type of relationship between the kinetic and thermodynamic parameters with a Bronsted coefficient of 0.37. One might ask why the values of $\ln(k_s \tau_L)$ were not correlated directly with ΔG_t^o. Unfortunately, the latter parameter is not available in many solvents[16] so that it is more practical to use the donor number to demonstrate this relationship. It should be noted that there is no correlation betwen $\ln(k_s\tau_L)$ and the permittivity parameter γ. Thus, if electron transfer is the r.d.s. in the reduction mechanism of Li^+ ion, the inner sphere contributions to $\Delta G_s^\ddagger$ predominate. On the basis of the evidence obtained earlier[48, 49], it is more likely that the r.d.s. involves ion transfer or adsorption. These conclusions are supported by the Bronsted relationship presented here.

When one corrects the standard rate constant for reduction of Na^+ (Table VI) by multiplying by the solvent relaxation time τ_L, one obtains a corrected kinetic parameter in hexamethylphosphoramide which is greater than that in acetonitrile. This kinetic parameter does not correlate with either the permittivity parameter γ or the DN. It follows that solvent relaxation phenomena are probably not important in determining the pre-exponential factor of the standard rate constant for this reaction. In fact, the Na^+ ion is much heavier than Li^+ and more weakly solvated so that it does not fill the criterion given by van der Zwan and Hynes[9] (see eq. (14)). On the basis of the reported values of $\ln k_s$ and ΔG_t^o, the Bronsted relationship for this reaction is

$$\Delta G_s^{\ddagger} = \text{constant} + 0.18 \ \Delta G_s^o \qquad (27)$$

The fact that the Bronsted coefficient is smaller is attributed to the weaker solvation of Na^+ with respect to Li^+. Thus, it is concluded that the electroreduction of Na^+ is governed by a r.d.s. similar to that for Li^+ but without a solvent dynamical effect in the pre-exponential factor.

In conclusion, the results presented show clearly a major difference in the solvent dependence of the standard rate constant for amalgam formation with respect to that for simple electron transfer. The analysis presented supports the conclusions reached earlier[47-49] that the r.d.s. in the mechanism of alkali metal reduction is ion movement in the double layer and not electron transfer. It would be interesting to examine solvent effects on other amalgam formation reactions especially those involving divalent caations such as the alkaline earth metals and transition metal ions such as Cd^{++} and Zn^{++}. Although some data exist in the literature for kinetic parameters in non-aqueous solvents, further work in more solvents needs to be carried out before an analysis of solvent effects can be performed.

The Transfer Coefficient

In order to assess the transfer coefficient obtained in electrode kinetic data, one must be able to correct the experimentally observed value α_{ex} for the double layer effect to obtain the apparent value α_a. As pointed out above, the double layer correction normally involves the assumption that the reaction site is on the o.H.p. and that the potential at that site is equal to the average potential on that plane, ϕ^d. Since the reaction site during electron transfer may not be on the o.H.p., or the reactant may move during the r.d.s., the apparent transfer coefficient is not necessarily equal to the intrinsic transfer coefficient. This problem has been considered in detail elsewhere both with respect to electron transfer[32] and amalgam formation reactions[14], and is not considered further here. The discussion in this section is limited to the intrinsic transfer coefficient, α, which is the quantity of theoretical interest with respect to the intersection of the free energy surfaces for the reactant and product states.

According to the theory of electron transfer[15,40], the intrinsic transfer coefficient for a simple reduction reaction is given by the equation

$$\alpha = 0.5 + \frac{F\ (\phi^m - \phi^m - \phi^r)}{8\ \Delta G^*} \qquad (28)$$

where ϕ^r is the potential at the reaction site. Thus, at the formal potential in the absence of double layer effects, α is predicted to be 0.5. The dependence of α on overpotential results from the assumption that the free energy surfaces in the direction of the reaction coordinate are parabolic.[15,50] The latter feature of the theory has been examined for the electroreduction of organic molecules in non-aqueous media and some evidence in its support has been presented.[51] When one changes the solvent, ΔG^* also changes so that the curvature in corrected Tafel plots is expected to be solvent dependent. However, this is a very minor effect for the reactions considered here, the curvature being difficult to detect experimentally for most simple electron transfer reactions. For systems in which the inner sphere reorganizational energy is solvent dependent, such as metal ions with solvent molecules as ligands, the dependence of α on potential should be greater. According to eq. (28), at the formal potential, α is independent of the nature of the solvent. This result expresses the fact that the reactant and product are in essentially the same environment as far as estimation of the outer sphere contribution to the reorganizational free energy is concerned. Very few data are available in which the apparent transfer coefficient is reported in several solvents. Fawcett and Jaworski[52] reported values of α_a for the reduction of p-dicyanobenzene in five non-aqueous solvents, the average value being 0.51 ± 0.07. The fact that α_a is close to 0.5 suggests that the charge center of the anion radical produced by electron transfer is close to the o.H.p. In the case of data for the electroreduction of anthracene[52], α_a is equal to 0.65 ± 0.03. In this case, the charge center of the product is probably in the diffuse layer so that the apparent transfer coefficient is larger than the intrinsic value (see eq. (13)). Unfortunately, other authors[2-6] who have studied organic redox reactions in a number of solvents did not report values of the transfer coefficient so that further examination of this topic is not possible at present.

The symmetry in the free energy surfaces for reactant and product which is predicted for electron transfer reactions with small values of ΔG^*_{is}, is not expected for amalgam formation reactions in which the r.d.s. involves a major change in atmosphere of the product with respect to that of the reactant. One such elementary step is adsorption in which the metal ion moves from a site where it is fully solvated by solvent molecules to the interface where it is partially solvated by solvent molecules and partially by mercury atoms. When the free energy barrier is asymmetrical, the intrinsic transfer coefficient is given by[53]

$$\alpha = \frac{k_i^{1/2}}{k_i^{1/2} + k_f^{1/2}} + \frac{k_i F (\phi^m - \phi^m - \phi^r)}{2(k_i^{1/2} + k_f^{1/2})^2 \Delta G^*} \qquad (29)$$

where $2k_i$ is the force constant describing the vibrational properties of the free energy surface for the reactant, and $2k_f$, that for the product. It is easily seen that when $k_i = k_f$, eq. (29) reduces to the expression for α for a symmetrical barrier (eq. (28)). On the other hand, if k_i is different from k_f, α is not equal to 0.5 at the standard potential. For instance, when $k_i = 10$

k_f, $\alpha = 0.76$ at the standard potential in the absence of double layer effects. The existence of an asymmetrical free energy barrier was used to explain the anomalously high values of α_a observed for the reduction of Cu(I) at mercury in acetonitrile.[53] In this system the reactant is strongly bound to the solvent acetonitrile so that the free energy surface describing it could be much steeper than that describing the product in an adsorption step. However, it is difficult to separate double layer effects from effects related to the shape of the free energy barrier. If the r.d.s. is indeed adsorption, then one expects α_a to be significantly larger than α because the process occurs in the inner layer.[14]

Kinetic studies of the reduction of alkali metal[46-49] and alkaline earth metal ions[54] in non-aqueous media have shown that the apparent transfer coefficient varies significantly with the nature of the solvent, and the background electrolyte. Thus, very low values of α_a were found for the reduction of K^+ and C_s^+ in hexamethylphosphoramide whereas a value of unity was obtained for the reduction of Li^+ in acetonitrile in the presence of tetrabutylammonium perchlorate. No trend is apparent in the transfer coefficient when the solvent is changed for a given reactant. This observation is undoubtedly due to the fact that the nature of the r.d.s. and its location in the double layer can change with solvent due to a corresponding change in the strength of solvation of the reactant. Thus, the fact that the apparent transfer coefficient contains a double layer contribution makes interpretation of this kinetic parameters much more difficult than in the case of simple electron transfer. Much more work on double layer effects for these reactions must be carried out before an attempt to identify the nature of the r.d.s. and estimate the intrinsic values of α can be made. It seems also clear that the kinetic information must be supplemented by spectroscopic information regarding reactant location and solvation before a better understanding of the transfer coefficient can be achieved.

Discussion

On the basis of the results analyzed in this paper, it is concluded that solvent dynamical effects are important for electron transfer reactions, and in some cases, for ion transfer reactions. In assessing these conclusions, one should keep in mind the fact that the solvent reorganizational time τ_L is a quantity which is often imprecisely available on the basis of data reported in the literature. This is mainly due to the fact that ε_∞ was often obtained by a long extrapolation of dielectric dispersion data obtained in a frequency range which was not sufficiently high. Thus, values of ε_∞ for fast solvents such as acetonitrile and nitromethane are probably correct to an order of magnitude only. It should also be recognized that the values of τ_L used in analyzing the kinetic data are those for the pure solvent. There is clear evidence in the literature[57-59] that dielectric relaxation parameters depend on the nature and concentration of the dissolved electrolyte. Thus, an improved assessment would result if τ_L values specific to each system were available. In most cases, authors have studied solvent effects using a fixed background electrolyte. However, when the electrolyte is changed it is clear that the kinetic parameters change as well.[2,48] This observation is undoubtedly due to changes in both double layer effects, and the effect of the ions in the vicinity of the reaction site on local dielectric relaxation phenomena. Unfortunately, too few data are available for the dielectric properties of polar solvents in the presence of electrolytes. The availability of more data would do much to clarify the role of the solvent in determining the standard rate constant.

In a previous paper[52], it was shown that ln k_s for the electroreduction of p-dicyanobenzene in five non-aqueous solvents decreased linearly with increase in the solvent's acceptor number. It was argued that this correlation demonstrated the role of local solvation effects in determining the value of the free energy of activation for electron transfer. However, the analysis presented ignored solvent effects on the formation of the activated complex. When one compares values of AN and τ_L for the solvents chosen in this study, it is readily apparent that a fortuitous linear correlation exists between these quantities. Thus, the highest value of k_s was observed in dimethylacetamide which has the lowest acceptor number highest value of k_s was observed in dimethylacetamide which has the lowest acceptor number and fastest relaxation time, whereas the lowest value of k_s was found in N-methylformamide which has the highest values of AN and τ_L for the solvent's considered. However, it is readily apparent from the data presented in Table I that, in general, there is no correlation between AN and τ_L. This study[52] demonstrates the need to choose solvents carefully in carrying out investigtions of solvent effects in electrode kinetics. Addition of one or two solvents to the study which do not follow the fortuitous correlation between AN and τ_L would clarify whether results for this system are in agreement with those discussed above.

Finally, it should also be emphasized that the kinetic experiments which are discussed in this paper are difficult to carry out precisely. Each solvent must be carefully purified by specific procedures since small levels of impurities can result in serious errors in the heterogeneous rate constant. Often, the rate constants fall in a high range with respect to experimental techniques[61] available. In addition, the electrochemical cell and electrode configuration must be carefully designed to avoid problems with iR drop.[60] In this regard, a.c. admittance techniques are ideally suited to measuring fast electrode kinetics. These experiments also provide the necessary capacitance data for estimating double layer effects when the admittance of the background electrolyte alone is measured.

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Table I. A Summary of Permittivity, Dielectric Relaxation, and Solvation Parameters for Aprotic Solvents[a]

Solvent	Relative Permittivity			Debye Relaxation	Donor	Acceptor
	Static ε_s	Infrared ε_{ir}	Visible ε_{op}	Time τ_D, ps	Number DN	Number AN
Acetone (AC)[62]	20.7	~2	1.839	3.3	17.0	12.5
Acetonitrile (AN)[63]	37.5	~2	1.800	3.3	14.1	18.9
Benzonitrile (BN)[64]	25.2	3.85	2.328	38.0	11.9	15.5
Dichloroethane (DCE)[65]	10.36	2.4	2.080	6.9	0	16.7
Dimethylacetamide (DMA)[66]	37.8	4.5	2.061	12.8	27.8	13.6
Dimethylformamide (DMF)[72]	36.7	3.0	2.040	13.8	26.6	16.0
Dimethylsulfoxide (DMSO)[71]	46.7	5.3	2.182	18.9	29.8	19.3
Hexamethylphosphoramide (HMPA)[59]	30.0	3.3	2.123	80	38.8	10.6
Nitrobenzene (NB)[64]	34.8	4.1	2.403	45.3	4.4	14.8
Nitromethane (NM)[67]	35.8	~2	1.903	3.9	2.7	20.5
Propylene Carbonate (PC)[68]	64.9	2.6	2.019	43	15.1	18.3
Pyridine (PY)[69]	12.3	2.3	2.273	6.9	33.1	14.2
Tetramethylurea (TMU)[70]	23.1	4.5	2.100	31	29.6	-

[a] All quantities in this table except ε_{ir} and τ_D are taken from the compilations of Marcus.[16]

The literature sources for ε_{ir} and τ_D are cited after each solvent.

Table II. Double Layer Parameters in Various Solvents at an Electrode Charge Density of -10 μC cm^{-2} and Electrolyte Concentration of 0.1M.

Solvent	Static Dielectric Constant ε_s	Gouy-Chapman Constant A, μC cm^{-2}	Diffuse Layer Potential Drop ϕ^d,V	Accelerating Factor[a] $\exp(-0.5\ f\ \phi^d)$
Acetone	20.7	0.95	-0.121	10.53
Acetonitrile	37.5	1.28	-0.106	7.86
Dimethylsulfoxide	46.7	1.43	-0.101	7.13
Formamide	111	2.20	-0.080	4.74
N-methylformamide	182	2.80	-0.069	3.83
Propylene carbonate	66.1	1.70	-0.093	6.05
Water	78.3	1.85	-0.088	5.54

[a] Accelerating factor for a reaction in which a molecule (z_A=0) is reduced to its anion radical at the o.H.p. with an intrinsic transfer coefficient of 0.5.

Table III. Potential of Zero Charge at the Mercury/Non Aqueous Solution Interface[a]

Solvent	Potential of Zero Charge	
	E_o, V[b]	ϕ_o^m, V[c]
Acetone (AC)[d]	-0.210	-0.670
Acetonitrile (AN)[e]	-0.250	-0.622
Dimethylformamide (DMF)[e]	-0.198	-0.691
Dimethylsulfoxide (DMSO)[e]	-0.278	-0.717
Ethanol (EtOH)[d]	-0.230	-0.640
Formamide (F)[e]	-0.448	-0.729
Methanol (MeOH)[d]	-0.300	-0.670
N-methylformamide (NMF)[e]	-0.335	-0.732
Propylene carbonate (PC)[e]	-0.273	-0.601

[a] The electrolyte was 0.1 M $LiClO_4$ in all cases.

[b] Measured with respect to an aqueous SCE.

[c] Measured with respect to the standard potential for the ferrocene / ferrocenium couple.

[d] Estimated from p.z.c. data given by Damaskin and Kaganovich[28] and half-wave potential data for the reduction of ferrocene.[30]

[e] Data obtained by Sahami and Weaver.[31]

Table IV. Kinetic Data for the Oxidation of 1,4-Diaminobenzene in Aprotic Solvents together with Solvent Relaxation Time and Donor Number

Solvent	Standard Rate Constant[a] k_S, cm s^{-1}	Longitudinal Relaxation time[b] τ_L, ps	Donor Number DN
Acetonitrile	0.22	0.2	14.1
Dimethylformamide	0.082	1.3	26.6
Dimethylsulfoxide	0.074	2.4	29.8
Propylene carbonate	0.055	2.6	15.1
Nitrobenzene	0.035	3.1	4.4
Hexamethylphosphoramide	0.017	8.9	38.8

[a] Data reported by Opallo.[5]

[b] Calculated from the parameters given in Table I using eq. (15).

Table V. Kinetic Data for the Reduction of Li^+ in Aprotic Solvents together with Solvent Relaxation Time and Donor Number

Solvent	Standard Rate Constant[a] k_s, cm s^{-1}	Longitudinal Relaxation Time τ_L, ps	Donor Number DN
Acetonitrile	0.15	0.2	14.1
Tetrahydrofuran	0.019	0.8	20.0
Propylene carbonate	0.01	2.7	15.1
Dimethylformamide	4.7×10^{-4}	1.3	26.6
Dimethylsulfoxide	1.3×10^{-4}	2.4	29.8
Hexamethylphosphoramide	1.4×10^{-7}	8.8	38.8

[a] Data tabulated by Baranski et al.[47]

[b] Calculated from the parameters given in Table I using eq. (15); the parameters for tetrahydrofuran are given by Saar et al.[41]

Table VI. Kinetic Data for the Electroreduction of Na^+ at Hg in Aprotic Solvents together with Solvent Relaxation Time and Donor Number

Solvent	Standard Rate Constant[a] k_s, cm s^{-1}	Longitudinal Relaxation Time[b] τ_L, ps	Donor Number DN
Acetonitrile	0.57	0.2	14.1
Dimethylformamide	0.09	1.3	26.6
Dimethylsulfoxide	0.054	2.4	29.8
Hexamethylphosphoramide	2.3×10^{-2}	8.8	38.8

[a] Data reported by Baranski and Fawcett.[48]

[b] Calculated from the parameters given in Table I using eq. (15).

Legends for Figures

Figure 1. Model for passage of a reacting metal ion through the compact region of the double layer. The solvent (dimethylformamide), predominant base electrolyte ion (tetraethylammonium cation) and reactant (sodium ion) are represented as hard spheres with the following radii; DMF = 0.34, TEA^+ = 0.40, and Na^+ = 0.095 nm. Positions 'a', 'b', and 'c' correspond to passage of the reactant from a fully solvated ion at its distance of closest approach (position 'c') to an adsorbed species at the interface (position 'a').

Figure 2. Formal potential for the reduction of phenazine at mercury in eight different aprotic solvents on the ferrocene / ferrocenium ion scale[24] plotted against the solvent's acceptor number. The abbreviations for the solvents are defined in Table I.

Figure 3. Formal potential for the oxidation of 1,4-diaminobenzene at platinum in eight different aprotic solvents on the ferrocene / ferrocenium ion scale[5] plotted against the solvent's donor number. The abbreviations for most of the solvent's are defined in Table I; otherwise, THF = tetrahydrofuran and TMS = tetramethylene sulphone

Figure 4. Half-wave potential for the reduction of Cd^{++} at mercury in 13 aprotic solvents on the bis(biphenyl)chromium (I)/(O) scale,[25] plotted against the solvent's donor number. The abbreviations for most of the solvents are defined in Table I; otherwise, BL = butyrolactone, DEA = diethylacetamide, DEF = diethylformamide, and PN = propionitrile.

Figure 5. Plot of the solvent corrected kinetic parameter $\ln (k_s \tau_L / \gamma^{1/2})$ against the permittivity parameter γ using data for the electrooxidation of 1,4-diaminobenzene at platinum in six aprotic solvents.[5]

Figure 6. Plot of the solvent corrected kinetic parameter $\ln (k_s \tau_L / \gamma^{1/2})$ against the permittivity parameter γ using data for the electroreduction of the cobaltacenium cation at mercury in seven aprotic solvents.[6]

Figure 7. Plot of the solvent corrected kinetic parameter $\ln (k_s\tau_L)$ against the donor number using data for the electroreduction of Li^+ at mercury in six aprotic solvents.[47]

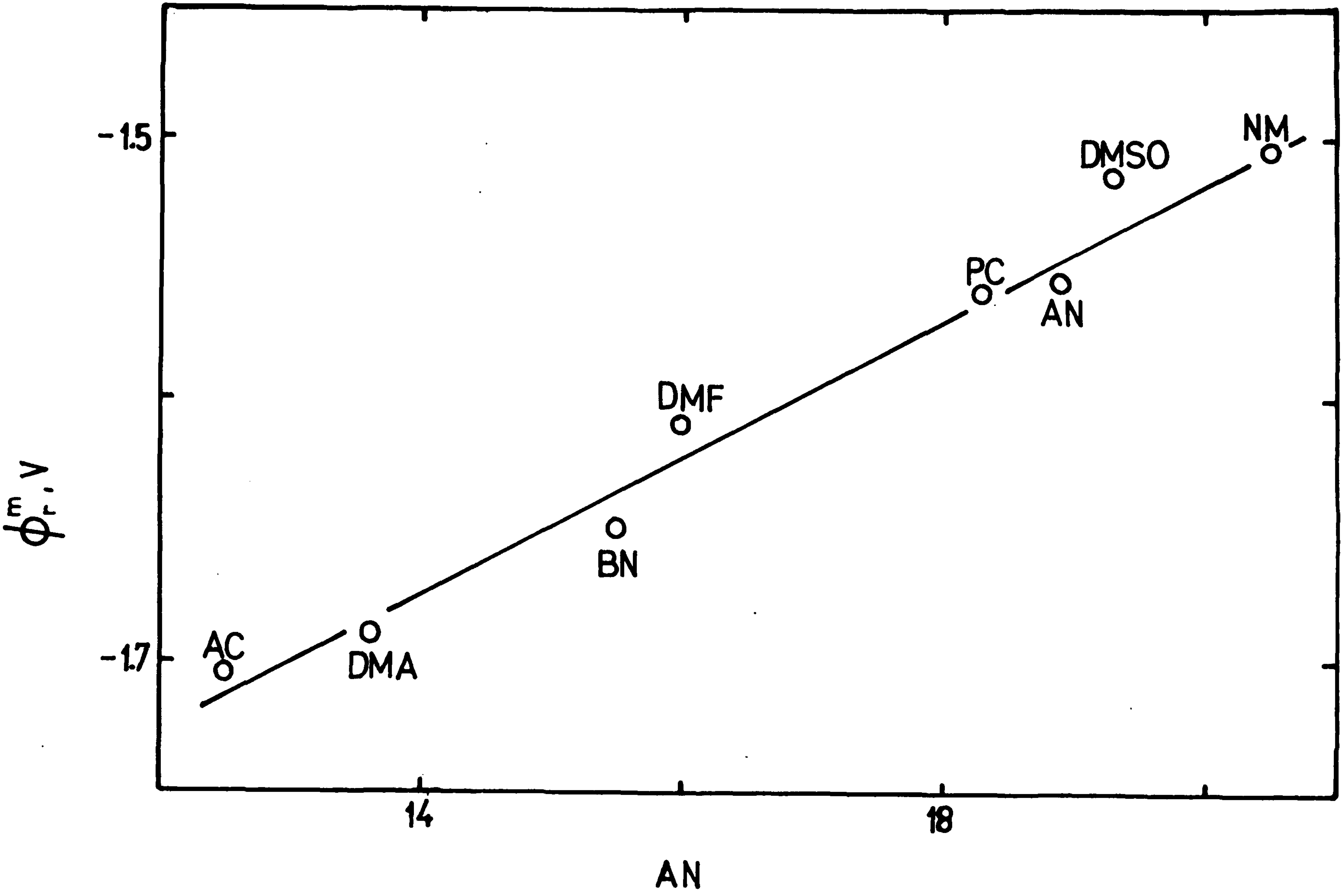
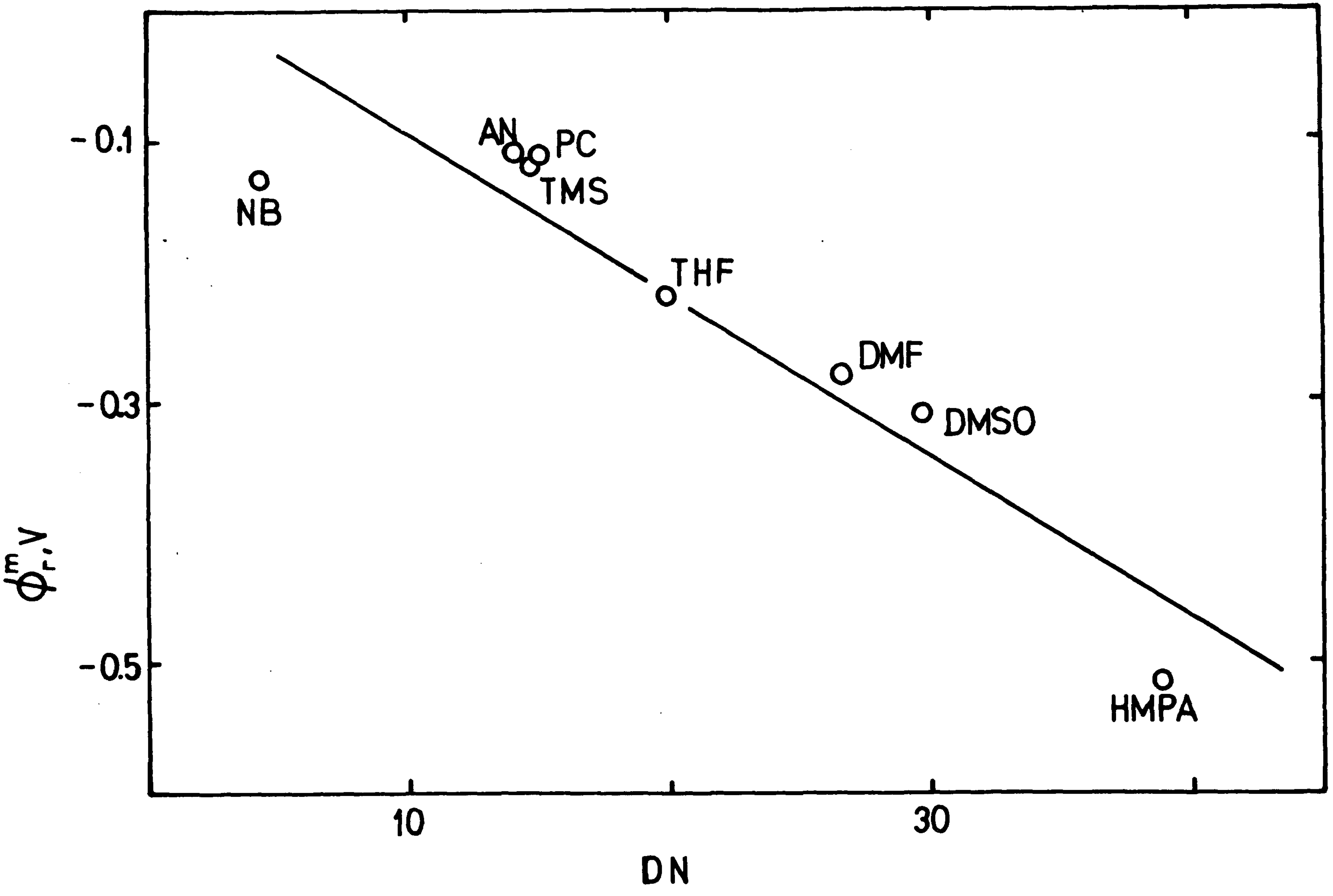


Fig 2


-0.1
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-0.5
ϕ_r^m,V
10
30
DN
NB
AN
PC
TMS
THF
DMF
DMSO
HMPA

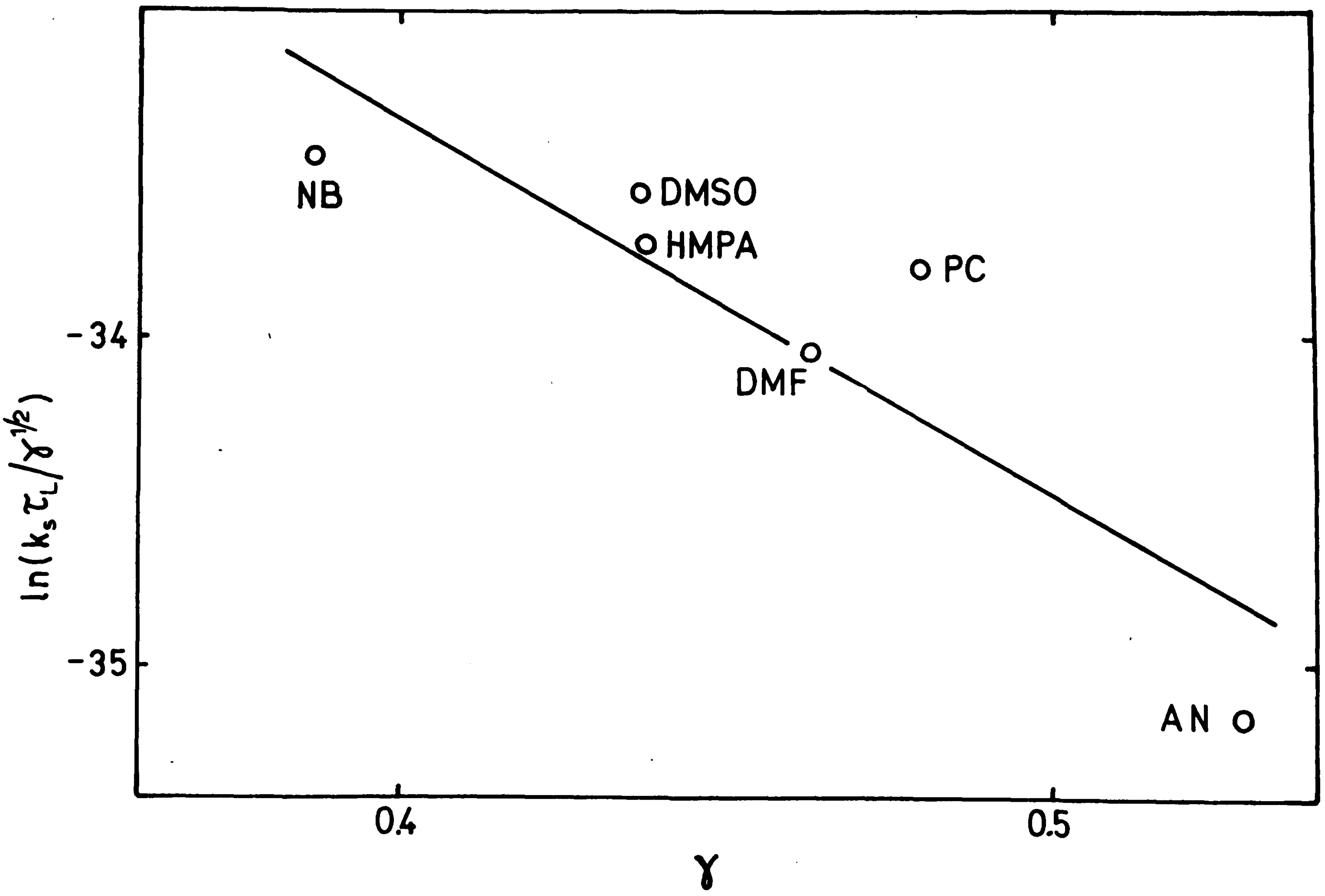
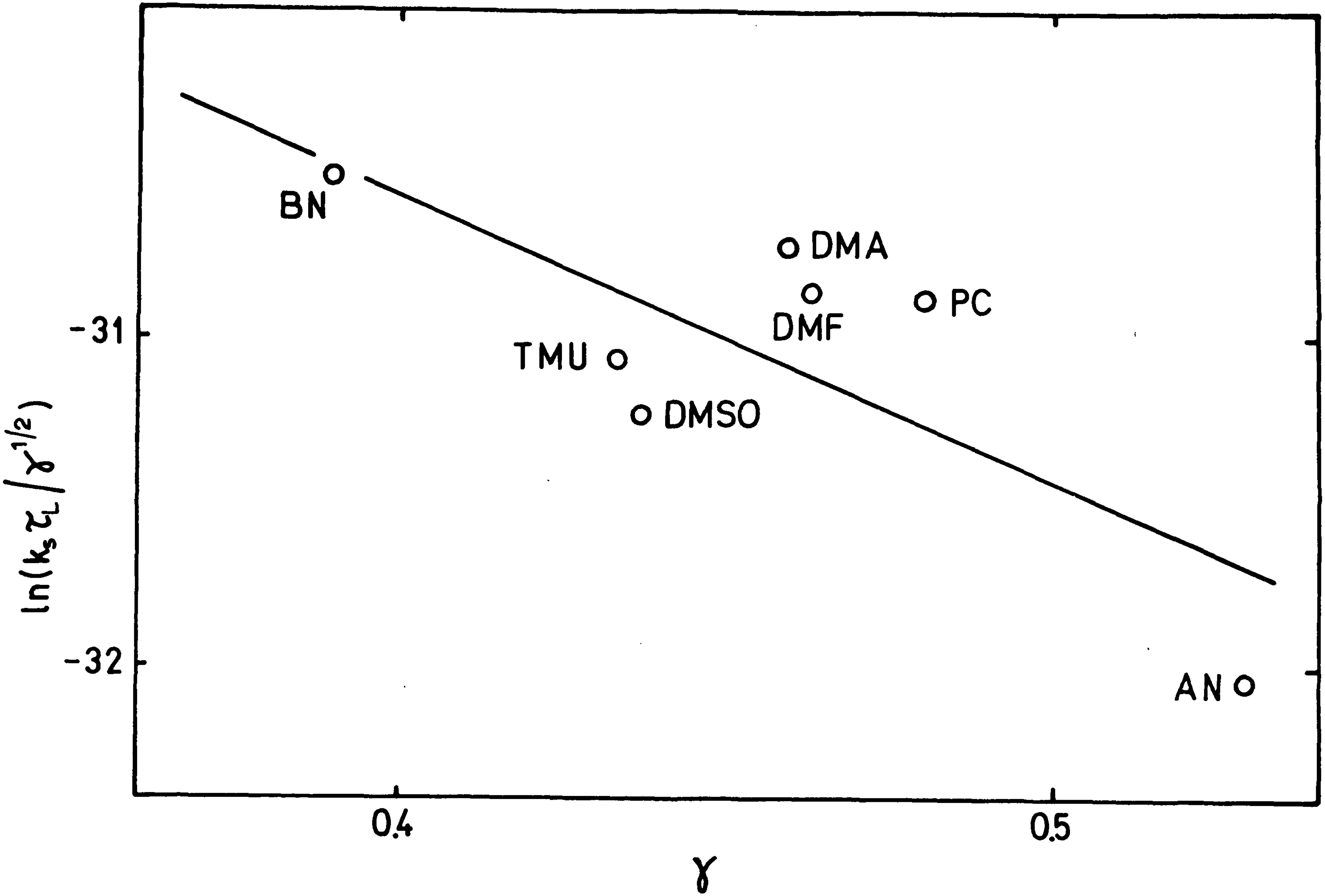


Fig 5


BN
DMA
DMF
PC
TMU
DMSO
AN
-31
-32
0.4
0.5
$\ln(k_s \tau_L / \gamma^{1/2})$
γ