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Electron Transfer Reactions

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Prepared for Publication

in

Journal of Electroanalytical Chemistry

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August 12, 1988

REPORT DOCUMENTATION PAGE	L REPORT NO. 6	2.	1. Recipient's Accession No.

4. Title and Subtitle
The Analysis of Solvent Effects on the Kinetics of Simple Heterogeneous Electron Transfer Reactions

5. Report Date August 12, 1988

6.

7. Author(s) W.R. Fawcett and C.A. Foss, Jr.

8. Performing Organization Rept. No.

9. Performing Organization Name and Address
Department of Chemistry
University of California
Davis, CA 95616

10. Project/Task/Work Unit No.

11. Contract(C) or Grant(G) No.
(C) N00014-87-K-0541
(G)

12. Sponsoring Organization Name and Address
Office of Naval Research
800 N. Quincy
Arlington, VA 22217-5000

13. Type of Report & Period Covered

14.

15. Supplementary Notes
Prepared for publication in:

16. Abstract (Limit 200 words)

A method for separating the solvent dependence of the pre-exponential factor from that in the free energy of activation is described for adiabatic electron transfer reactions in which the inner sphere contribution to the activation energy is much less than the outer sphere contribution. The analysis is applied to data published in the literature in which the heterogeneous electron transfer rate constant was measured in at least 4 different solvents. The resulting kinetic parameters are discussed with respect to current theory.

17. Document Analysis   a. Descriptors

b. Identifiers/Open-Ended Terms

c. COSATI Field/Group

18. Availability Statement

19. Security Class (This Report) Unclassified

21. No. of Pages

20. Security Class (This Page)

22. Price

(See ANSI-Z39.18)   See Instructions on Reverse   OPTIONAL FORM 272 (4-77)

Preliminary Note

The Analysis of Solvent Effects on the Kinetics

of Simple Heterogeneous Electron Transfer Reactions

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Introduction

Solvent effects on electron transfer reactions have been the subject of considerable interest in recent years. For a simple heterogeneous process such as

$$A + e \iff B \qquad (1)$$
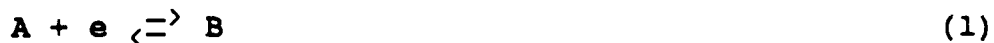
where both A and B are present in an electrolyte solution, one may recognize four effects of the solvent on the kinetic parameters. Firstly, the standard potential for the reaction depends on the free energy of solvation of reactant and product, and changes with the charges on these species and the extent to which a given polar solvent can solvate the reactant and product species [1]. The second way in which the solvent plays a role is through the double layer effect according to which the concentration of the reactant at the reaction site and the potential drop experienced by the electron during transfer are a function of the local electrostatic field, which, in turn, depends on the charge density on the electrode and the dielectric properties of the electrolyte solution in the double layer [2]. Thirdly, the solvent affects the free energy of activation for reaction (1), especially through the dependence of the outer sphere contribution to solvent reorganization on the dielectric properties of the surrounding medium [3]. This aspect has been of particular interest in recent years, many workers having examined the validity of the elegant though perhaps simplistic Marcus dielectric continuum treatment [4-8]. Finally, the

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dynamic properties of the solvent determine the frequency which
the activated complex is formed, and further, the frequency with
which such a complex successfully decays to the product
configuration. This aspect is expressed in the pre-exponontial
part of the standard rate constant, and was considered in detail
in two recent seminal papers by Calef and Wolynes [9,10]. Since
the appearance of their work, a number of experimental studies of
solvent effects on heterogeneous electron transfer reactions
involving organic and organometallic molecules have been reported
in the literature [11-15]. The systems chosen were ones in which
the component of the free energy of activation due to internal
reorganization was small so that the effect of the solvent on the
observed standard rate constant was easily seen. Particularly
impressive is the work of Opallo [14] who studied the
electrooxidation of 1,4-diaminobenzene in twelve different
solvents and obtained kinetic parameters in a range where good
precision is possible. Opallo also demonstrated in this work,
and in an earlier study with Kapturkiewicz [13] that solvent
effects are clearly different for protic and aprotic solvents.
Nonetheless, a clear correlation between solvent dynamical
properties and the standard rate constant was demonstrated.
Similar results were obtained by Weaver and coworkers [12,15],
who examined the reduction kinetics of various metallocene
complexes and iron cyclooctatetraene tricarbonyl in a series of
aprotic and protic solvents.

At first inspection, the results of both studies
mentioned above show no indication of the connection between the

rate constant and the solvent reorganizational energy estimated from the Marcus treatment. This result is surprising given the excellent agreement between absorption maxima for intramolecular charge transfer in mixed valence complexes and the Marcus predicted outer sphere reorganization energies [4]. In the present communication we consider in detail the general expression for the rate constant proposed by Calef and Wolynes [9,10], and present an analysis that demonstrates the validity of their form of the pre-expontial factor as well as the Marcus dielectric continuum treatment for the activation free energy.

The Analysis

According to the encounter pre-equilibrium model [9,10], the standard rate constant corrected for double layer effects is given by

$$k_{sc} = \kappa K_p \nu_n \exp(-\Delta G^*/RT) \tag{2}$$

where κ is the electronic transmission coefficient, K_p, the equilibrium constant for precursor complex formation, ν_n, the nuclear frequency factor, and ΔG^*, the reorganizational free energy of activation. 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 [16,17], and an outer sphere contribution ΔG^*_{os} given by [3]

$$\Delta G^*_{os} = \frac{N_0 e^2}{32\pi\epsilon_0} \left(\frac{1}{a} - \frac{1}{R}\right) \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right) \tag{3}$$

where N_0 is Avogadro's number, e, the charge on the electron, a, the radius of the reactant represented as a sphere, R, the distance of the charge center of the reactant from its image in the electrode, ϵ_{op}, the optical dielectric constant, ϵ_s, the static dielectric constant, and ϵ_0, the permittivity of free space. This estimate of ΔG^*_{os} is based on the Born model, and inherits some key simplistic assumptions, namely, that the solvent is a structureless continuum and that there is no spatial

dispersion of the dielectric constant at distances beyond the reactant radius.

For systems in which $\Delta G^{*}_{os} \gg \Delta G^{*}_{is}$, the nuclear frequency factor is described by the overdamped solvent relaxation model and is given by [9,12]

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

where τ_L is the longitudinal solvent relaxation time. This quantity can be determined from the dielectric properties of the solvent as follows:

$$\tau_L = \frac{\tau_D \epsilon_\infty}{\epsilon_s} \tag{5}$$

τ_D, is the usual Debye relaxation time and ϵ_∞, the dielectric constant of the solvent at infrared frequencies. Values of τ_L have been estimated for a large number of aprotic solvents commonly used in non-aqueous electrochemistry [13,15] and are summarized in Table 1. It is clear that there is considerable variation in τ_L, namely, from 0.2 ps in acetonitrile (AN) to 8.9 ps in hexamethylphosphoramide (HMPA). It is important to point out that eq. (4) is strictly applicable only to solvents for which τ_L is greater than 1 ps [9]. Data discussed in this paper certainly include solvents that do not meet this criterion, a point which is examined further below.

On the basis of the models described here, it follows that the corrected standard rate constant k_{sc} depends on the nature of the solvent in two ways, namely, through variation of the nuclear frequency factor, ν_n, and variation in the outer sphere contribution to the free energy of activation, ΔG^*_{os}. When one examines the data published to date [11-15], it is clear that variation due to the nuclear frequency factor predominates. Thus, Opallo [14] obtained an excellent linear correlation between the logarithm of the standard rate constant and the logarithm of the longitudinal solvent relaxation time τ_L using data for the oxidation of 1,4-diaminobenzene in eight different aprotic solvents, in spite of the fact that ΔG^*_{os} is changing at the same time. This result is not surprising when one considers the fact that τ_L changes by a factor of 40 for the solvents considered by Opallo [14] whereas $(\epsilon^{-1}_{op} - \epsilon^{-1}_s)$, the solvent dependent part of ΔG^*_{os}, changes only by a factor of 1.4. In addition, there is no correlation between τ_L and $(\epsilon^{-1}_{op} - \epsilon^{-1}_s)$ (see Table 1). In analyzing their data, previous authors have attempted to confirm the validity of the encounter pre-equilibrium model [9,10] by estimating values of k_{sc} on the basis of the above equations and comparing the estimates with experimental results. This procedure is rather unsatisfactory because it requires that one assume values for the parameters a and R in order to estimate ΔG^*_{os}, and a value for κK_p in order to estimate the rate constant, k_{sc}. Weaver [12,15] compared calculated and observed values of k_{sc} by plotting the logarithm of one quantity against the logarithm of the other. In such a

comparison, the choice of κK_p affects only the intercept of the plot whereas the value chosen for the distance parameter aR/(R-a) affects the slope and the correlation coefficient in a least squares analysis.

It seemed to us that these data provided an opportunity to test the validity of the Marcus formulation [3] for ΔG^*_{os} in so far as its solvent dependence is concerned. Combining eqs. (2)-(4), and defining

$$\delta = \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \tag{6}$$

and

$$g = \frac{N_0 e^2}{32 \pi \epsilon_0 RT} \left(\frac{1}{a} - \frac{1}{R} \right) \tag{7}$$

one obtains the expression

$$k_{sc} = \frac{\kappa K_p}{\tau_L} \left(\frac{g\delta}{4\pi} \right)^{1/2} \exp(-\Delta G^*_{is}/RT) \exp(-g\delta) \tag{8}$$

Rearranging, one may write

$$\ln \left(\frac{k_{sc}\tau_L}{\delta^{1/2}} \right) = \ln \left[\kappa K_p \left(\frac{g}{4\pi} \right)^{1/2} \right] - \frac{\Delta G^*_{is}}{RT} - g\delta \tag{9}$$

It follows that a plot of $\ln(k_{sc}\tau_L/\delta^{1/2})$ against δ should be linear with a slope of $-g$. Furthermore, if ΔG^*_{is} is known, one

may es⁺ᵢmate the product κK_p from the intercept. Thus, the present analysis assumes that the dependence of the preexponential factor on the solvent parameters τ_L and δ is correct as described by the encounter pre-equilibrium model [9,10], and examines the dependence of the kinetic data corrected for part of the solvent effect on the dielectric parameter δ in order to assess the validity of the Marcus expression for the outer sphere contribution to the reorganizational free energy. Details of our analysis of data from the literature [11-15] are now discussed in detail.

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*This equation was used previously by Harrer et al. [23] to demonstrate solvent effects on the rate constant for homogeneous electron transfer between tetracyanoquinodimethane and its anion radical. However, these authors did not analyze the parameters obtained from the linear fit.

Results and Discussion

The above analysis was applied to four sets of kinetic data for systems in which the kinetic parameters had been obtained in at least four aprotic solvents using the same base electrolyte [13-15]. In all cases, a good linear correlation was obtained between the solvent corrected kinetic parameter $\ln(k_{sc}\tau_L/\delta^{1/2})$ and the permittivity parameter δ with a negative slope. While previous work has demonstrated that the solvent exerts its influence on electron transfer primarily through the nuclear frequency factor ν_n, the present analysis makes it clear for the first time that the Marcus· expression for ΔG^*_{os} is also valid for heterogeneous electron transfer.

Values of the slope and intercept for plots of published data [11-15] are summarized in Table 2; in addition, the plots obtained for the 1,4-diaminobenzene [14] and cobaltacenium systems [15] are shown in Figures 1 and 2, respectively. In all cases, the magnitude of the slope yields very reasonable values for the reactant size-distance parameter, $aR/(R-a)$. However, the values obtained here are quite different from the values assumed by Opallo [14] and Weaver et al. [15]. For instance, in his analysis, Opallo took the reactant radius a for 1,4-diaminobenzene to be 0.34 nm, as determined from diffusion coefficient data using the Stokes-Einstein equation. Assuming the imaging distance R to be infinity, the value of $aR/(R-a)$ is 0.34 nm which compares with the value, 0.62 nm obtained by the present analysis. Similarly, Weaver et al. [15] assumed a = 0.38 nm and R = ∞ in analyzing data for the cobaltacenium system.

According to the present analysis aR/(R-a) is equal to 0.85 nm, a considerably higher value. These results are significant in two respects. Firstly, in selecting values for the parameter aR/(R-a), previous authors have essentially doubled the magnitude of ΔG^{*}_{0s}. Secondly, if one calculates R on the basis of their assumed molecular radii a, which are certainly reasonable, it is apparent that R is finite and the order of 0.7 nm. Indeed, the assumption that R = ∞ is a precarious one theoretically, since the electronic transmission coefficient approaches zero for large values of R, and the reaction can no longer be considered adiabatic. In any case, some disagreement between the true and calculated values of aR/(R-a) is not unexpected considering the fact that the Marcus model assumes simple spherical ions are involved in the reaction. Thus, an improved estimate of ΔG^{*}_{0s} can be obtained if a species such as the cation radical formed from 1,4-diaminobenzene is represented as a collection of spheres rather than a single sphere [18].

For both the 1,4-diaminobenzene and cobaltacenium systems, estimates of ΔG^{*}_{is} have been made so that values of κK_{p} could be extracted from the intercepts of the plots shown in Figs. 1 and 2. For 1.4-diaminobenzene, Grampp and Jaenicke [19] estimated ΔG^{*}_{is} to be 0.9 kJ mol^{-1}. Accordingly, from the value of the intercept, the estimate of κK_{p} is 0.48 ± 0.48 pm. While the error in the estimate is large, κK_{p} is still two orders of magnitude smaller than the value of 60 pm proposed by Hupp and Weaver [20] and assumed by Opallo [14]. For the cobaltacenium case, when ΔG^{*}_{is} is estimated to be 1.0 kJ mol^{-1} [15], κK_{p} is

2.7 ± 2.8 pm. While larger than that for the 1,4-diaminobenzene case, this result also suggests that previous estimates of κK_p are too high.

In assessing the above results one should keep in mind the fact that the longitudinal relaxation time τ_L, which has the major influence on the observed rate constants, varies with the nature and concentration of the supporting electrolyte [21-22]. The values cited previously [13-15] and summarized in Table 1 are those for the pure solvent. On the basis of the kinetic data obtained by Kapturkiewicz and Opallo [11] for the electroreduction of nitromesitylene, it is clear that the standard rate constant after double layer correction varies significantly with the nature of the cation of the electrolyte. Thus, the value of $k_{s,c}$ obtained in tetrabutylammonium perchlorate was always smaller than that found in tetraethylammonium perchlorate. This observation can be attributed to a corresponding decrease in the viscosity of the electrolyte solution, and thus, in the value of τ_L. Considering the fact that few dielectric relaxation data are available, it is clear that one should only attempt the type of analysis presented here for systems in which the concentration and nature of the base electrolyte is kept constant when the solvent is changed. Then, the assumption made is that the actual values of τ_L parallel those observed in the pure solvent, and that the difference between these quantities affects only the values of the intercept of plots such as those presented here. It should also be remembered that the values of τ_L recorded for some solvents are

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rather imprecise. Although reasonably precise values of the Debye relaxation time τ_D are available for most solvents, the values of ϵ_∞ are sometimes uncertain due to the fact that the frequency range for the dielectric measurements was not sufficiently high. The availability of more data for dielectric relaxation in electrolyte solutions would do much to improve the situation.

It should also be pointed out that in both the present analysis and previous work [11-15], it has been assumed that the image distance R is independent of the solvent. If the reaction site is on the outer Helmholtz plane, this assumption is strictly not valid since the thickness of the inner layer depends on the size of the solvent molecule. This is obviously connected to the other assumption implicit in this analysis, namely, that κK_p is also a solvent independent parameter. The electronic transmission coefficient κ is certainly distance sensitive, and hence, solvent sensitive as well if the reaction site is on the outer Helmholtz plane or further out in the diffuse layer. With the present data, however, we can find no connection between the molecular volumes for a given solvent and deviation from linearity.

Finally, as a comment on the general validity of the overdamped solvent relaxation expression for ν_n, we note the fact that some of the solvents in which longitudinal relaxation is rapid, namely, acetonitrile, dichloromethane, and tetrahydro-furan, to which eq. (4) is not strictly applicable, seems to fall nicely on line with the present analysis. Perhaps further work

will determine whether this is due to the effect of the supporting electrolyte on τ_L, or to a fortuitous shortcoming of the theory.

We are presently considering solvent effects on homogeneous outer sphere electron transfer reactions. Meanwhile, it is hoped that the present work will help stimulate future work and solidify experimental strategies for the study of solvent effects in heterogeneous electron transfer reactions.

Acknowledgement

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Table 1. A Summary of Permittivity and Dielectric Relaxation Parameters for Aprotic Solvents.*

Solvent	Relative Permittivity			Debye Relaxation Time, τ_D, ps	Longitudinal Relaxation Time τ_L, ps	Permittivity Parameter $(1/\varepsilon_{op} - 1/\varepsilon_s)$
	Static, ε_s	Infrared, ε_∞	Visible, ε_{op}			
Acetonitrile (AN)	37.5	2	1.800	3.3	0.2	0.529
Nitromethane (NM)	35.8	2	1.903	3.9	0.2	0.498
Acetone (AC)	20.7	2	1.839	3.3	0.3	0.495
Dichloromethane	8.93	2.5	2.020	1.5	0.4	0.383
Pyridine (PY)	12.3	2.3	2.273	6.9	1.3	0.359
Dimethylformamide (DMF)	36.7	4.5	2.040	11.0	1.3	0.463
Dimethylacetamide (DMA)	37.8	4.5	2.038	12.8	1.5	0.464
1,2-dichloroethane	10.4	2.4	2.080	6.9	1.6	0.385
Dimethylsulfoxide (DMS)	46.7	5.7	2.182	19.5	2.4	0.437
Propylene Carbonate (PC)	66.1	4.1	2.019	43	2.7	0.480
Nitrobenzene (NB)	34.8	4.1	2.403	45.6	5.4	0.387
tetrahydrofuran (THF)	7.58	2.3	1.974	16	4.9	0.375
benzonitrile (BN)	25.2	3.9	2.328	38	5.9	0.390
tetramethylurea (TMU)	23.1	4.5	2.100	31	6.0	0.433
sulpholane (TMS)	43.3		2.196		6.5	0.432
hexamethylphosphoramide (HMPA)	30.0	3.3	2.123	80	8.8	0.423

*Values of ε_s and ε_{op} are from the compilation of Marcus [1]. Values of ε_∞ and τ_D were taken from the papers of Opallo [14] and Weaver et al. [12, 15] who cite the original literature.

Table II. Summary of Parameters Found in Fitting Equation (9) to Kinetic Data for Heterogeneous Electron Transfer

Reactant	Number of Solvents	Slope	Intercept	Regression Coefficient	Distance Parameter $aR/(R-a)$ nm	Preexponential Factor κKp pm
1,4-diaminobenzene (0/+)[14]	7	-11.3 ± 2.2	3.4 ± 1.0	0.92	0.62 ± 0.12	0.5 ± 0.5
cobaltacenium (+/0)[15]	8	-8.3 ± 2.3	5.0 ± 1.0	0.82	0.85 ± 0.24	3 ± 3
cyclooctatetraenirqn tricarbonyl (0/-)[15]	4	-12.9 ± 1.1	8.4 ± 0.5	0.99	0.55 ± 0.05	-
phenothiazene (0/+)[13]	6	-7.5 ± 3.3	1.7 ± 1.6	0.75	0.93 ± 0.41	-

Legends for Figures

Figure 1.   Plot of the solvent corrected kinetic parameter $\ln (k_{sc} \tau_2 / \delta^{1/2})$ against the permittivity parameter $1/\epsilon_{op} - 1/\epsilon_s$ using data for the electrooxidation of 1,4-diaminobenzene at platinum in seven aprotic solvents [14].

Figure 2.   Plot of the solvent corrected kinetic parameter $\ln (k_{sc} \tau_2 / \delta^{1/2})$ against the permittivity parameter $1/\epsilon_{op} - 1/\epsilon_s$ using data for the electroreduction of the cobaltacenium cation in eight aprotic solvents [15].
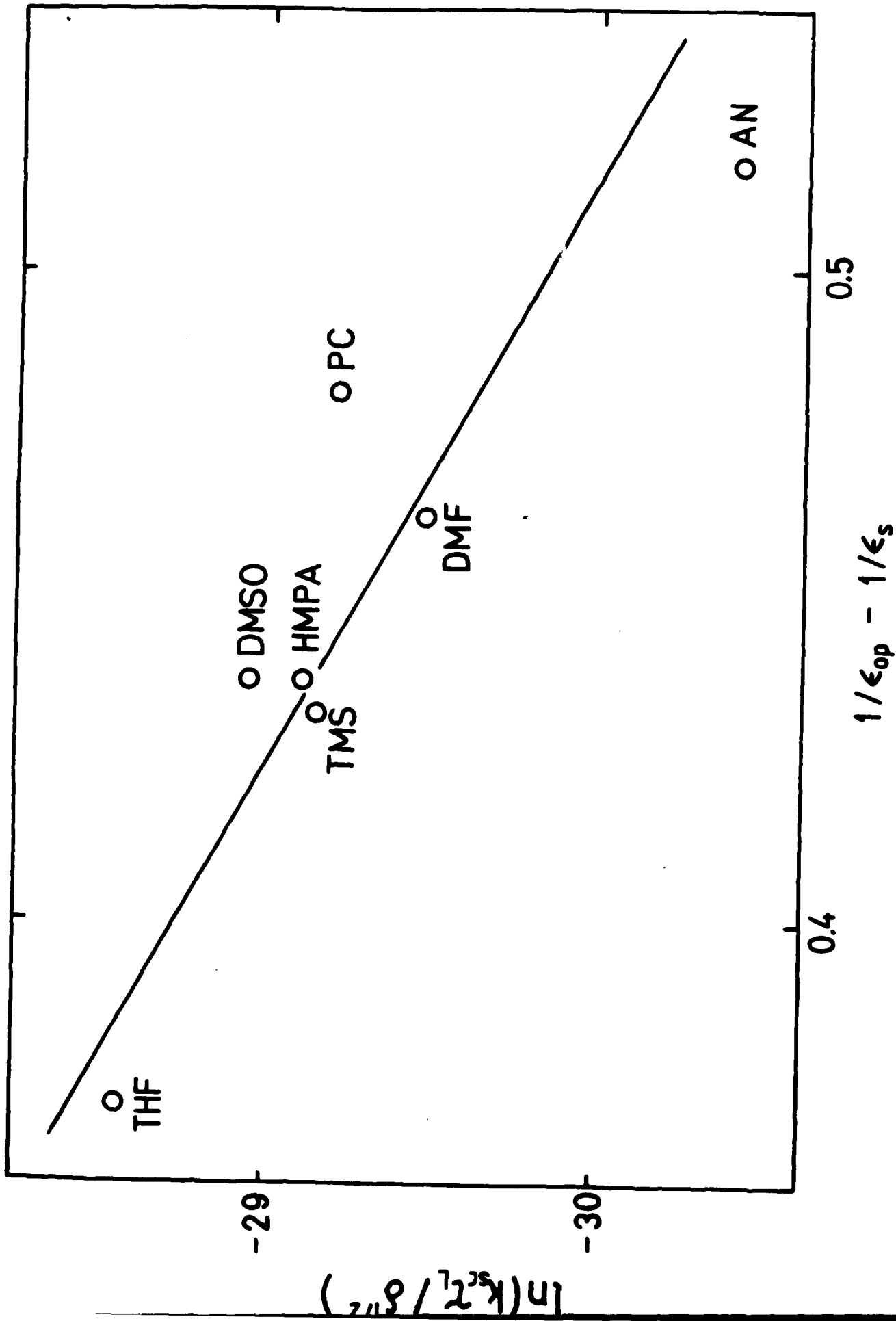
Fig. 1   Fawcett & Foss

The x-axis is labeled $1/\epsilon_{op} - 1/\epsilon_s$ with values 0.4 and 0.5 marked.

The y-axis is labeled $\ln(k_{ec}\tau_L/\delta^{1/2})$ with values -29 and -30 marked.

Data points: THF, DMSO, HMPA, TMS, DMF, PC, AN

$\ln(k_{sc}\tau_L/\delta^{1/2})$

$1/\epsilon_{op} - 1/\epsilon_s$

-26

-27

0.4

0.5

O CH$_2$Cl$_2$
O BN

DMA O
DMF O

TMU O
O DMSO

O PC

AN O