Solvent effects in simple fast electron transfer reactions

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The kinetics of the one-electron reduction of *p*-dicyanobenzene and the oxidation of nickelocene have been studied by ac voltammetry in different aprotic solvents at mercury and platinum ultramicroelectrodes. The observed electron transfer rate constants have been corrected for the double-layer effect. The solvent dependences of the electron transfer rate constants and activation enthalpy are interpreted within the context of contemporary theory. The charge transfer process was found to be perfectly adiabatic for both studied systems. Solvent dynamic and Gibbs activation energy effects on the rate constants were also investigated.

In recent years, considerable progress has been made toward understanding the role played by the solvent in the thermodynamics and kinetics of homogeneous and heterogeneous electron transfer processes. It is now generally recognized 1-3that the solvent can affect the Gibbs activation energy (ΔG^*) and the pre-exponential factor of the rate constant. The preexponential factor, according to contemporary theory, depends on the solvent's dielectric relaxation properties through its longitudinal relaxation time, τ_L .⁴ On the other hand the solvent influences the Gibbs activation energy through its outer-sphere component ($\Delta_{os} G^*$). Estimation of $\Delta_{os} G^*$ requires the assumption of a solvation model such as the Born model.^{2,3} Recently it has been suggested⁵ that the estimation of $\Delta_{os} G^*$ can be improved by using the mean spherical approximation (MSA) for ionic solvation at static frequencies.

The encounter-pre-equilibrium model, on which modern theory is based, has been examined for a number of heterogeneous redox systems.^{2,3} Generally, for fast electrochemical charge transfer processes a good linear correlation between ln k_s and ln τ_L is observed indicating that the dynamic properties of the solvent on the pre-exponential factor predominate in the kinetic solvent effect. However, this kind of analysis considers only the dynamic contribution to the solvent effect. A more complex analysis, which assumes the classical expression for $\Delta_{os} G^*$ based on the Born solvation model, and also adiabacity of the electron transfer process, was proposed by Fawcett and Foss.^{6,7} Another way to deal with the separation of the two solvent effects is to correct the rate constant for the outer-sphere activation barrier, and then examine the dependence of the corrected quantity on τ_L .^{8,9}

The analysis of activation parameters obtained from the temperature dependence of the rate constant is another valuable tactic for extracting information about solvent effects on electron transfer.^{2,3} The linear relation between the experimentally obtained activation enthalpy ($\Delta_{ex}H^*$) and the enthalpy associated with the temperature dependence of τ_L (ΔH_L) can also provide useful information about the adiabacity of fast electron transfer reactions.

In the present paper the results of a study of solvent effects on the electroreduction of *p*-dicyanobenzene (DCB) and electrooxidation of nickelocene $[Ni(cp)_2]$ are presented. Precise data were obtained by using ultramicroelectrodes in ac voltammetric experiments.^{10,11} The analysed kinetic data obtained at Hg electrodes are corrected for the double-layer effect. The solvent effect on both the kinetic and thermodynamic data is analysed and compared for the two systems.

Experimental

Chemicals

Analytical grade solvents: dimethylformamide (DMF), acetonitrile (AcN), dichloromethane (DCM), 1,2-dichloroethane (DCE), butyronitrile (BuN), propylene carbonate (PC), acetone (AC) and dimethyl sulfoxide (DMSO) were dried over calcium hydride for one day and then distilled under vacuum. Tetrabutylammonium perchlorate (TBAP) was precipitated from an aqueous solution of tetrabutylammonium hydroxide (Aldrich) with perchloric acid, washed using water and then dried under vacuum. 1,4-Dicyanobenzene (DCB) and nickelocene (both Aldrich) were used without further purification.

Electrochemical measurements

All electrochemical measurements were performed using a three electrode system. The reference electrode was Ag/0.1 M $AgNO_3$ in DMF. The DMF was separated from the analysed solution using molecular sieves type 3A (BDH Chemicals). The silver solution was replaced daily because of the instability of Ag⁺ to photoreduction in DMF. The stability of the reference electrode was examined by recording the ferrocene oxidation potential in the studied solvents as a function of time. The formal potential of the ferrocene-ferrocenium system was found to be stable for 3 to 5 h, depending on the solvent. The counter electrode was made from a platinum wire. The ultramicroelectrodes which served as working electrodes were manufactured by sealing the metal wire (Goodfellow Metals Ltd, UK) into a soft glass capillary using a Bunsen burner flame. The capillary was then cut perpendicularly to its length and the surface was polished using extra fine carborundum paper followed by 0.3 µm alumina. Electrical contacts were made using silver epoxy (Johnson Matthey Ltd, UK). Hemispherical mercury drop electrodes were prepared by electrodeposition of a sufficient amount of mercury from an aqueous solution of $1 \text{ M Hg}_2(\text{ClO}_4)_2$ in HClO₄ onto a polished Au disk electrode. The time of mercury deposition was controlled by computer. In the study of double-layer capacity and in the determination of standard potentials and

diffusion coefficients, a hanging mercury drop electrode with a surface area of 0.0094 cm^2 was used. The solution were deaerated for 20 min with argon prior to the electrochemical measurements.

In dc and ac voltammetric experiments an EG&G Princeton Applied Research (PAR) Model 273 and PC 6300 AT&T computer were used. In dc voltammetric measurements positive feedback iR compensation was employed. The admittance against electrode potential data were obtained for different ac frequency values in the potential range of the faradaic process. The background in- and out-of-phase admittances were fitted before and after the peak of the faradaic process to a third-order polynomial by a least-squares method and the background admittances under the peak were thereby numerically evaluated. The solution resistance and double-layer capacity were found from the background in- and out-ofphase admittance at the peak potential of the faradaic process. Admittance data obtained as a function of potential were analysed by the de Levie and Husovsky method.12 Prior to the actual experiments, the optimum frequency range was obtained from a simulation program.¹⁰ The ac voltammetric experiments on a hanging mercury drop electrode (HMDE) were carried out in order to determine the double-layer capacity of the Hg electrode in the studied solutions. Potentials of zero charge (E_z) were obtained polarographically from the zero charge current (DCM, DMF, DCE, DMSO and PC) or from the minimum of the differential capacity in solutions of low supporting electrolyte concentration (AcN and AC). The classical Frumkin correction of the kinetic parameters for double-layer effects¹³ was performed.

Constant temperatures down to -55 °C were obtained using a methanol bath in a Dewar flask whose temperature was controlled with an immersion cooler.

Results

The process of DCB electroreduction was studied using a 5 µm radius mercury electrode by ac and steady-state voltammetry. From the steady-state voltammograms the diffusion coefficient (D) and formal potentials (E_f) of DCB in different solvents were calculated. A standard size HMDE was used for diffusion coefficient determination and good agreement between the results obtained from both techniques was observed. The kinetic parameters (k_s and α_{ex}) obtained on the basis of an analysis of the admittance vs. potential curve were corrected for the double-layer effect. The values obtained for diffusion coefficients, formal potentials, and the observed and corrected kinetic parameters are summarized in Table 1 (Fig. 1). On the basis of the Stokes-Einstein equation a DCB radius (r_{DCB}) equal to 0.33 nm was calculated. The value of r_{DCB} estimated from the density data¹⁴ is 0.35 nm. There is also good agreement between the observed standard rate constant of electron exchange in the $DCB^{0/-}$ system presented in this paper and that presented in earlier work.¹⁵ The process of DCB electroreduction takes place at potentials much more negative than the E_z of mercury in the studied solvents and consequently a strong double-layer effect is observed. Correcting k_s to account for the double-layer effect yields values of k_{sc} much greater than the observed values.



Fig. 1 Diffusion coefficient of DCB in various solvents plotted against the reciprocal viscosity. 0.05 M TBAClO₄ was the background electrolyte.

The dependence of the rate constant on temperature was also studied. Assuming that the pre-exponential factor depends on $T^{-1/2}$ the value of $\Delta_{ex}H^*$ was calculated on the basis of plots of $\ln(k_sT^{1/2})$ vs. 1/T (Fig. 2).¹⁶ The experimental values of the activation enthalpy obtained from the slope of these plots are collected in Table 1.

A study of solvent effects on the kinetics of charge transfer in the $[Ni(cp)_2]^{0/+}$ system was also carried out. The formal potential of this system is close to the E_z for the mercury electrode in the solvents used. However, the changes of doublelayer capacity in the potential range of $[Ni(cp)_2]$ oxidation are still significant and lead to k_{sc} values much greater than the observed values of k_s ; the latter were obtained at a hemispherical mercury electrode with a 25 µm radius. The changes in



Fig. 2 Plots of the $(k_s T^{1/2})$ against reciprocal of temperature for the DCB reduction at Au/Hg (5 μ m) electrode. 0.05 M TBAClO₄ as the background electrolyte.

Table 1 Diffusion coefficients of DCB, formal potentials, charge transfer coefficients, observed and corrected standard rate constants and experimental activation enthalpy of $DCB^{0/-}$ system. 0.05 M TBAP, Au/Hg(5 μ m)

solvent	$D/10^{-5} \text{ cm}^2 \text{ s}^{-1}$	$E_{\rm f}/{\rm mV}$ vs. Fc ^{0/+}	α _{ex}	$k_{\rm s}/{\rm cm~s^{-1}}$	$k_{\rm sc}/{\rm cm~s^{-1}}$	$\Delta_{ex} H^*/kJ \text{ mol}^{-1}$
AcN	2.8	-1990	0.55	0.95	28.5	18.5
AC	3.2	-2081	0.53	0.75	24.6	15.0
DCM	2.35	-2158	0.54	0.54	14.5	15.6
DMF	1.08	-2015	0.51	0.27	5.2	20.8
PC	0.46	- 1995	0.52	0.14	3.2	25.5

double-layer capacity in the potential range of the studied faradaic process make the analysis of admittance data difficult and leads to a decrease in the precision with which the kinetic parameters may be determined. Typical curves of in- and out-of-phase admittance as a function of potential for the electrooxidation of [Ni(cp)₂] in AcN are presented in Fig. 3(a). The observed and corrected values of kinetic parameters of the $[Ni(cp)_2]^{0/+}$ system for different solvents are presented in Table 2. Additional studies of the electron transfer kinetics of the $[Ni(cp)_2]^{0/+}$ system were carried out at a Pt electrode with a 12.5 µm radius. In this case, the changes of capacity within the potential range of the faradaic process are much lower than for the Hg electrode [Fig. 3(b)]. The kinetic parameters obtained at a Pt electrode at 295 K and the thermodynamic parameters of activation calculated from the slope of plots of $\ln(k_s T^{1/2})$ vs. 1/T are summarized in Table 2. The observed rate constants for the $[Ni(cp)_2]$ electrooxidation at the Pt electrode are higher than those at Hg, but they are much lower than the corrected standard rate constants at the mercury electrode. The results of a study of double-layer capacity at a Pt electrode in AcN solutions containing LiClO₄ show that the E_z of the Pt electrode is only about 120 mV more positive than E_z at Hg.¹⁷ The changes of E_z are much lower than predicted by the difference in work functions of Pt



Fig. 3 Plots of the in- and out-of-phase admittance as a function of potential for the oxidation of 0.6 mM $[Ni(cp)_2]$ in AcN containing 0.1 M TBAClO₄ at Au/Hg (25 µm) (a) and Pt (12.5 µm) (b) electrode. The frequency was equal to 25 (a) or 45 kHz (b).

and Hg.¹⁸ It can be expected that for a Pt electrode the standard potential of the $[Ni(cp)_2]^{0/+}$ system is still more positive than the zero charge potential and the observed k_s values are lower than they would be after double-layer correction. In addition, the sequence of observed k_s for Pt and Hg is in agreement with the changes in E_z for these electrodes.

From the slope of the linear relationship between diffusion coefficient, calculated from the limiting steady-state current, and the inverse of solvent viscosity, the radius of $[Ni(cp)_2]$ was found to be equal to 0.37 nm. This agrees well with estimates of this parameter for other metallocenes.⁸

Analysis and Discussion

The solvents were chosen for the study so that a relatively wide range of longitudinal relaxation times and outer-sphere Gibbs activation energies would be involved in the solvent effect investigation. The τ_L values vary from 0.2 ps for AcN to 2.7 ps for PC. Considerable variation of the $\Delta_{os} G^*$ can also be noticed. The outer-sphere reorganization energy, determined on the basis of MSA model, changes by about 40% for both studied systems. For the solvents studied in this paper the ln τ_L and $\Delta_{os} G^*$ parameters are not collinear. Correlation coefficients equal to 0.592 and 0.481 were found for eight solvents selected for the study of the charge transfer process in the [Ni(cp)_1^{0/+} system and five solvents chosen for the DCB^{0/-} system, respectively.

The kinetic data were analysed assuming that the corrected standard rate constant can be expressed as³

$$k_{\rm sc} = A\tau_{\rm L}^{-\Theta} \exp[-(\Delta_{\rm os} G^* + \Delta_{\rm is} G^*)/RT]$$
(1)

where A is the portion of the pre-exponential factor which is approximately independent of solvent nature, and Θ is a fraction between 0 and 1 which depends on the degree of reaction adiabacity. One of the important problems in the analysis of the solvent effect is the estimation of Θ . Recognizing that an important contribution to this effect comes from $\Delta_{os} G^*$, eqn. (1) can be rewritten as follows:

$$\ln k_{\rm sc} + \Delta_{\rm os} G^*/RT = \ln A - \Delta_{\rm is} G^*/RT - \Theta \ln \tau_{\rm L}$$
 (2)

This suggests that plots of the LHS vs. In $\tau_{\rm L}$ should be linear giving a slope equal to Θ . In order to make such plots $\Delta_{\rm os} G^*$ was estimated according to the MSA model⁵ using the parameters tabulated in earlier papers.^{8,19} These estimates are recorded in Table 3. Good linear plots were obtained for both systems studied. For the $[Ni(cp)_2]^{0/+}$ system, the slope yields a value of Θ equal to 1.19 for the data at a Hg electrode with a correlation coefficient of 0.975. The slope is significantly higher for the data at Pt (1.46) but since these data were not corrected for the double-layer effect, not much importance is given to this result. In the case of the DCB^{0/-} system, the estimate of Θ from a similar plot is 1.24. Both results are higher than the expected maximum value of 1 for this parameter. We attribute this to the additional dependence of the pre-

Table 2 Charge transfer coefficients, observed and corrected standard rate constants and experimental activation enthalpy of $[Ni(cp)_2]^{0/+}$ system. 0.1 M TBAP

solvent	Au/Hg(25 μm)			Pt(12.5 μm)			
	α _{ex}	$k_{\rm s}/{\rm cm~s^{-1}}$	$k_{\rm sc}/{\rm cm~s^{-1}}$	α _{ex}	$k_{\rm s}/{\rm cm~s^{-1}}$	$\Delta_{ex} H^*$	
AcN	0.54	0.71	4.0	0.47	2.0	18.4	
AC	0.53	0.55	4.2	0.51	1.8	17.1	
BuN	_			0.49	0.52	20.5	
DCM	0.50	0.40	4.5	0.50	1.4	18.4	
DMF	0.51	0.14	1.45	0.52	0.54	23.1	
DCE	0.47	0.25	3.0	0.51	0.8	18.8	
DMSO	0.51	0.10	0.92	0.52	0.2	26.3	
PC	0.51	0.055	0.42	0.49	0.12	30.1	

Table 3	Comparison of	f estimated an	d experimental	values of	f outer-sphere	reorganization	energy
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	DCB ^{0/-}				$[Ni(cp)_2]^{0/+}$	<i>v</i>) ₂] ^{0/+}
solvent	$\Delta_{\rm os} G^{*a}$	$\Delta_{\rm os} H^{* a}$	$\Delta_{\rm os} H^{* b}$	$\overline{\Delta_{\rm os}G^{*\ a}}$	$\Delta_{\rm os} H^{* a}$	$\Delta_{\rm os} H^{* b}$
AcN	21.2	20.2	13.7	16.1	14.7	14.0
AC	19.1	18.2	12.5	15.3	14.1	13.3
BuN	18.2	18.5	_	14.2	13.9	12.9
DCM	13.8 ^c	_	11.5	10.4°		11.1
DMF	17.5	18.3	14.2	14.0	13.1	13.6
DCE	14.5°			10.5°	_	10.9
DMSO	16.8	17.4		12.7	12.3	12.7
PC	17.8	17.2	12.7	13.8	13.2	13.2

^{*a*} In kJ mol⁻¹, estimated on the basis of MSA model. ^{*b*} In kJ mol⁻¹, calculated according to eqn. (7) using experimental values of the activation enthalpy. ^{*c*} Based on average values of the MSA δ_s parameter.

exponential factor on the solvent as discussed below. In the remaining analysis, Θ is assumed to be unity, that is, the reactions are assumed to be perfectly adiabatic.

In the case of adiabatic reactions, the pre-exponential factor can be specified more exactly³ so that

$$A\tau_{\rm L}^{-\Theta} = \kappa K_{\rm p} \tau_{\rm L}^{-1} \left(\frac{\Delta_{\rm os} G^*}{4\pi RT}\right)^{1/2} \tag{3}$$

where κ is the electronic transmission coefficient, and K_p is the encounter pre-equilibrium constant. It follows that eqn. (1) can be rewritten as

$$\ln \frac{k_{\rm sc}}{\Delta_{\rm os} G^{*1/2}} + \frac{\Delta_{\rm os} G^*}{RT} = \ln \left[\frac{\kappa K_{\rm p}}{(4\pi RT)^{1/2}} \right] - \frac{\Delta_{\rm is} G^*}{RT} - \ln \tau_{\rm L}$$
(4)

This equation demonstrates that there should be a linear relationship between the function of the LHS and $\ln \tau_L$ with a slope of unity. Plots for the data considered here with the best straight lines of unit slope are shown in Fig. 4. Good correlations, particularly for the $[Ni(cp)_2]^{0/+}$ system, are found with some scatter due to the experimental error involved in determining the fast electron transfer rate constants for these systems.

Analysis of the intercepts of these plots allows one to estimate κK_p provided independent estimates of $\Delta_{is} G^*$ are available. The inner-sphere reorganization energy can be calculated using the harmonic oscillator model. According to this model $\Delta_{is} G^*$ is expressed by the equation:

$$\Delta_{\rm is} G^* = 0.5 \sum f_{\rm is} \left(\frac{\Delta a}{2}\right)^2 \tag{5}$$

where Δa is the change in a given bond distance between the oxidized and reduced forms of the redox system and $f_{\rm is}$ is the force constant of this bond defined as:

$$f_{\rm is} = 4\pi^2 v_{\rm is}^2 \,\mu \tag{6}$$

 v_{is} is the frequency and μ is the reduced mass of the vibrating bond. For the electrooxidation of nickelocene it can be assumed that the only significant structural perturbation is the change in the metal-ring distance. For $\Delta a = 0.074 \ A^{20,21}$ and $v_{is} = 9.6 \ 10^{12} \ s^{-1}$,²² a value of $\Delta_{is} G^*$ equal to 2.7 kJ mol⁻¹ was calculated. Using this value of inner-sphere activation energy, the estimate of κK_p is 20.0 ± 12.2 pm. This value is only slightly lower than that predicted by Hupp and Weaver.²³ For DCB the data required for determination of the inner-sphere reorganization energy are not available and the κK_p was calculated assuming that $\Delta_{is} G^*$ is equal to zero. From the intercept of the linear relation predicted by eqn. (4) the estimate of κK_p is 400 pm on the basis of the corrected k_s values. This result is much higher than the expected value of 60 pm for this parameter. It can be attributed to an overestimation of the double-layer effect or the neglect of $\Delta_{is} G^*$. The process of DCB electroreduction takes place in a potential range very negative with respect to the E_z . A change in double-layer structure in this potential region in aprotic solvents containing tetraalkylammonium cations due to weak adsorption of the cations was reported recently.24,25 Therefore, the corrected values of standard rate constant are probably overestimated in this case, resulting in a high estimate of κK_{p} . In fact, the same analysis performed for the uncorrected values of the standard rate constant leads to an estimate of $\kappa K_{\rm p}$ equal to 14.7 ± 8.5 pm. The adsorption of tetrabutylammonium cations on the electrode surface may also be responsible for the somewhat weak correlation presented in Fig. 4(a) for the $DCB^{0/-}$ system. A particularly low value of the standard rate constant was observed in DCM in comparison to values of k_s obtained in other solvents. Since the relative permittivity of DCM is relatively low, ion pairing will be



Fig. 4 Plots of the logarithm of the corrected rate constant, $\ln[k_{sc}/(\Delta_{os} G^*)^{1/2}] + \Delta_{os} G^*/RT$ for the reduction of DCB at an Au/Hg (5 µm) electrode (a) and oxidation of $[Ni(cp)_2]$ at Pt Au/Hg (25 µm) (b) against the logarithm of the longitudinal relaxation time, $\ln \tau_L$. The straight lines were obtained for a slope equal to unity.

The solvent effect on the activation enthalpy was also investigated. Assuming that any contribution to the inner-sphere Gibbs energy of activation is equal to the corresponding enthalpic quantity and the Θ parameter is equal to unity, the following equation can be written:^{3.26}

$$\Delta_{\rm os} H^* = \Delta_{\rm ex} H^* - \Delta_{\rm is} H^* - \Delta H_{\rm L} \tag{7}$$

The observed enthalpy of activation, $\Delta_{ex} H^*$, was calculated on the basis of the temperature dependence on the standard rate constant uncorrected for the double-layer effect. An additional term related to the temperature dependence of the outer Helmholtz plane potential, ϕ^d , should be considered. According to Fawcett and Kováčová²⁶ this contribution is significant only in the potential range close to the zero charge potential. Since the process of DCB electroreduction takes place in a very negative potential range, the double-layer contribution can be neglected. However, the standard potential of the $[Ni(cp)_2]^{0/+}$ system is located relatively close to the zero charge potential of the platinum electrode and neglecting the double-layer term may lead to an error in the $\Delta_{os} H^*$ determination. However, on the basis of data obtained at Hg,²⁶ this contribution is not expected to be large and is also neglected.

The values of $\Delta_{os} H^*$ calculated according to eqn. (7) are presented in Table 3 and compared to the theoretical activation enthalpies estimated according to the MSA model using the parameters tabulated elsewhere.^{8,19} For the $[Ni(cp)_2]^{0/+}$ system it was assumed that the value of $\Delta_{is} H^*$ is equal to the value calculated earlier of $\Delta_{is} G^*$ (2.7 kJ mol⁻¹). For the $DCB^{0/-}$ system the outer-sphere activation enthalpy was calculated assuming that $\Delta_{is} \hat{H}^*$ is equal to zero. A good agreement between experimental and theoretical values of the activation energy is observed for the [Ni(cp)₂] electrooxidation process. In the case of the $DCB^{0/+}$ system the experimental values of activation enthalpy are much lower than those predicted by the MSA theory. The assumption about spherical symmetry of the reactant may be one of the reasons for the observed differences. This disagreement may also be related to the influence of tetraalkylammonium cations on the thermodynamics of the interface in this system because it occurs at very negative potentials where these cations have a large influence on the inner-layer structure. The minor contribution of excited high-frequency vibrational modes of DCB to the barrier of electron transfer may also be responsible for small values of $\Delta_{os} H^*$. According to Bixon and Jortner,^{27,28} the involvement of high-frequency vibrational states in the electron exchange process may dramatically decrease the activation barrier even for a process mainly controlled by the average reorganization energy.

Eqn. (7) suggests that a plot of $\Delta_{ex} H^*$ less the estimate of $\Delta_{os} H^*$ should be a linear function of ΔH_L with a slope equal to one and intercept equal to $\Delta_{is} H^*$. This kind of plot is presented in Fig. 5 for the $[Ni(cp)_2]^{0/+}$ system. The high scatter reflects the relatively large error involved in determining the experimental activation enthalpy. The estimate of $\Delta_{is} H^*$ from the intercept is 1.7 kJ mol⁻¹, a value which is close to the estimate of $\Delta_{is} G^*$ using the harmonic oscillator model.

The data presented in Table 3 show that the effect of activation entropy for the energy barrier of electron transfer is not very large. Assuming that the values of $\Delta_{os} H^*$ calculated according to eqn. (7) are close to values of the outersphere Gibbs activation energy a linear relation between $[k_{sc}/(\Delta_{os} H^*)^{1/2}] + \Delta_{os} H^*/RT$ and $\ln \tau_L$, predicted by eqn. (4), can be expected. A relatively good correlation was observed for the $[Ni(cp)_2]^{0/+}$ system (Fig. 6). From the intercept of the



Fig. 5 Plot of the difference between the experimental activation enthalpy, $\Delta_{ex} H^*$, and the MSA estimate of the outer-sphere contribution, $\Delta_{os} H^*$, for the $[Ni(cp)_2]^{0/+}$ system against the activation enthalpy for longitudinal relaxation, ΔH_L . The straight lines were obtained for a slope equal to unity. For DCM and DCE the values of $\Delta_{os} G^*$ were used.

best straight line of unit slope, an estimate of κK_p equal to 16.3 ± 12.4 pm is calculated. This value is very close to the κK_p parameter obtained on the basis of our analysis using the MSA values of $\Delta_{os} G^*$ (Fig. 4). The values of the κK_p parameter obtained for the [Ni(cp)₂]^{0/+} system agree very well with estimates of this parameter obtained using kinetic data for other metallocenes.^{8,29}

In summary, the data presented show that the solvent effect on electron transfer processes for the DCB^{0/-} and $[Ni(cp)_2]^{0/+}$ systems can be successfully described on the basis of the encounter pre-equilibrium model. From the analysis of the kinetic and thermodynamic data some general quantitative conclusions can be made: (i) both studied systems are perfectly adiabatic; (ii) a good correlation between the Gibbs energy barrier corrected parameter, $\ln [k_{sc}/(\Delta_{os} G^*)^{1/2}]$ $+ \Delta_{os} G^*/RT$, and the logarithm of the longitudinal relaxation time, $\ln \tau_L$, is observed for both studied systems; (iii) for the $[Ni(cp)_2]^{0/+}$ system relatively good agreement between experimental and theoretical values of the activation enthalpy calculated on the basis of MSA model is observed; (iv) our results show also that high-frequency ac admittance is a very



Fig. 6 Plot of the logarithm of the corrected rate constant, $\ln[k_{sc}/(\Delta_{os}H^*)^{1/2}] + \Delta_{os}H^*/RT$, for oxidation of [Ni(cp)₂] at Au/Hg (25 µm) against the logarithm of the longitudinal relaxation time, ln τ_{L} . The straight line was obtained for a slope equal to unity.

useful technique for the study of fast heterogeneous charge transfer processes.

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