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Heterogeneous Rate Parameters of Multi-Step Charge-Transfer Processes for 9,9′-Bianthryl-10,10′-dicarbonitrile. Application of ac Voltammetry with Unusual Phase-Angle Behavior

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Cyclic and ac voltammetric studies of a 9,9′-bianthryl-10,10′-dicarbonitrile/tetrabutylammonium hexafluorophosphate system in superdry aprotic solvents are presented. The rate parameters were obtained for successive one-electron transfer reactions at a hanging mercury drop electrode (HMDE) and/or a Pt disk electrode. The results of electrode processes were found to be in agreement with the predictions of the Marcus theory for heterogeneous charge-transfer reactions. Quite rare behavior of the phase angle of the Faradaic fundamental alternating currect was observed and is discussed in detail.

The first application of an ac impedance-bridge technique to studies of aromatic hydrocarbons in DMF was found by Aten and Hoytink.$^{1)}$ Studies of a series of nitrobenzene derivatives$^{2)}$ and stilbene as well as its derivatives by Peover and co-workers$^{3)}$ yielded kinetic data also using an impedance-bridge method. The results of these investigations revealed a successful quantitative correlation between the rate parameters and the predictions of the Marcus theory$^{4)}$ for electron-transfer kinetics, the activation energy of which arises from solvent molecule reorientation.

Geiger and Smith$^{5)}$ reported on the heterogeneous electron-transfer kinetic data obtained using ac polarographic techniques for some metal sandwich compounds in acetonitrile. Kojuma and Bard$^{6)}$ also applied an ac impedance method for a determination of the rate parameters of rapid electrode processes of some aromatic compounds in DMF.

There have been only few systematic studies of the electrochemical kinetics in characterizing the rate parameters associated with the electrode reactions of multiply-charged organic ions.$^{7—9)}$ This may be attributed to two limitations: One is the high reactivity of supercharged ions; the other is that difficulties in the classical measurement arise from the large uncompensated resistance in aprotic solvents. This work presents the results of kinetic measurements on highly charged 9,9′-bianthryl-10,10′-dicarbonitrile (DBA) in carefully purified and dried organic solvents. Modern instruments which allow precise measurements of the rate parameters were employed. A very rare behavior of the phase angle of the Faradaic alternating current was observed.

Experimental

Reagent-grade benzonitrile, propiononitrile and acetonitrile were further purified and dried according to a previous recommended method.$^{10)}$ Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) obtained from Fluka was recrystallized twice form pure ethanol and vacuum dried at 120 °C. DBA was synthesized by a method of Lohaus,$^{11)}$ and then chromatographed using an active Al_2O_3 column with a 1 : 1 mixture of toluene and cyclohexane.

For sample preparation and purification for electrochemical measurements in superdry aprotic solvents, a new type of cell was constructed (described elsewhere$^{12)}$).

In this cell, three electrodes were used: the working electrode was either a Metrohm production EA 290 hanging mercury drop electrode (HMDE) or a platinum disk electrode sealed in glass. The latter was well-polished using fine powdered Cr_2O_3, followed by diamond paste. The electrode was then washed twice with distilled water and pure ethanol, and dried in a vacuum. The reference electrode was Ag/AgCl, the potential of which was calibrated for each experiment against the reversible oxidation peak of ferrocene. A platinum wire was used as an auxiliary electrode.

Cyclic voltammograms obtained for the survey were recorded using an EG & G Princeton Applied Research potentiostat/galvanostat Model 273 equipped with both an IBM PC Model 30 computer and an EG & G PAR X-Y Recorder Model RE 0089. An EG & G Princeton Applied Research 5208 two-phase lock-in analyzer was used in conjunction with the 273 potentiostat/galvanostat to perform the shift in the phase angle, fundamental and second harmonic valtammograms (in-phase in quadrature components). The latter response (second harmonic) was obtained by multiplying a reference signal of the 5208 lock-in amplifier, as described elsewhere.$^{5)}$ Either a positive feedback or a current-interrupt circuitry, which was installed inside the Model 273, was used in all of the measurements to minimize any iR-drop effects. The peak-to-peak amplitude of the applied alternating potential used in this work was 10 mV, and the employed frequencies were in the 12—330 Hz range.

Results and Discussion

The electrochemical generation of both DBA tetraanions and the dications has been frequently investigated by the cyclic voltammetric method.$^{7)}$ The data obtained from the different mehtods, such as cyclic voltammetric anodic–cathodic peak separations of approximately 58 mV$^{16)}$ and low-frequency ac fundamental harmonic peak potentials, match the $E^{\mathrm{r}}_{1/2}$ of the second harmonic responses (in-phase and quadrature components). These were consistent with the nernstian (or at least nearly so) charge-transfer behavior. However, at sufficiently high frequencies, the kinetic effects of the heterogeneous charge transfer become evident, as shown by the $[\cot\phi]_{\max}-\omega^{1/2}$ linear profiles (ϕ and ω are the phase angle of the ac current relative to the applied ac potential and angular frequency, respectively) characteristic of the quasi-reversible process.[15]

The diffusion coefficient required to calculate the electrode rate parameters was determined from the dc polarographic limiting currents by the aid of the Ilkovic' equation.[8] For the second-harmonic Faradaic alternating current, one obtains the following expression:[9,14]

$$I(2\omega t) = \frac{2^{\frac{1}{2}} n^3 F^3 A C_o (\omega D_o)^{\frac{1}{2}} \Delta E^2 \sinh(j/2)}{16R^2T^2 \cosh^3(j/2)} \sin(2\omega t - \pi/4), \quad (1)$$

where $I(2\omega t)$ is the Faradaic second-harmonic alternating current; n the number of electrons transferred in heterogeneous charge-transfer step; F Faraday's constant; A the electrode suface area; C_0 the bulk concentration of the depolarizer; ω the angular frequency; D_0 the diffusion coefficient of the oxidized form; ΔE the amplitude of the applied alternating potential; R the gas constant; T the absolute temperature; and

$$j = \frac{nF}{RT}\left(E_{\mathrm{dc}} - E^{r}_{1/2}\right).$$

At $E_{\mathrm{dc}}=E^{\mathrm{r}}_{1/2}$ the second-harmonic current component ($I(2\omega t)$) equals zero. The α value, which is the charge-transfer coefficient ($\alpha=1-\beta$), can be determined using Eq. 2[15] from the potential of the maximum on the $\cot\phi-E_{\mathrm{dc}}$ plot and the $E^{\mathrm{r}}_{1/2}$ found from the precise zero-current locations of the in-phase and quadrature second-harmonic components (Eq. 1). Careful selection of suitable frequencies enables symmetrical negative and positive ac-current lobes to be obtained. Typical examples of such measurements are shown in Figs. 1B and 2A.

$$[E_{\mathrm{dc}}]_{\max} = E^{\mathrm{r}}_{1/2} + RT/nF \ln(\alpha/\beta) \quad (2)$$

The $\cot\phi$ of the ac fundamental faradaic current has its maximum value ($[\cot\phi]_{\max}$) at $E_{\mathrm{dc}}=[E_{\mathrm{dc}}]_{\max}$, where[15]

$$[\cot\phi]_{\max} = 1 + \{(2\omega D)^{1/2}/k_{\mathrm{s}}[(\alpha/\beta)^{-\alpha} + (\alpha/\beta)^{\beta}]\}. \quad (3)$$

Subsequent to obtaining diffusion coefficients and the α value by the foregoing procedures, the apparent heterogeneous reaction-rate constants (k_{s}) were calculated from the slopes of the $[\cot\phi]_{\max}-\omega^{1/2}$ profiles according to Eq. 3.

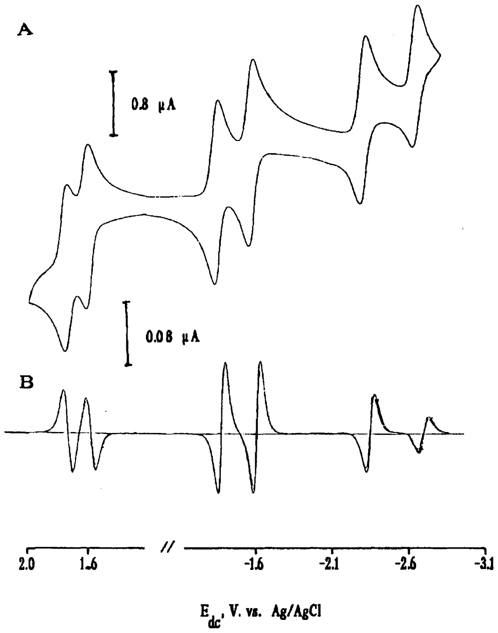

Fig. 1. Voltammograms of the DBA system. Conditions: 1.1×10^{-3} M DBA in propiononitrile/0.1 M $\mathrm{TBAPF_6}$ at 253 K at a Pt-disk electrode ($A=1.54\times10^{-2}$ cm^2) vs. Ag/AgCl. A) CV for dc scan rate of 50 mV s^{-1}. B) Phase-selective second harmonic (quadrature component) for dc scan rate o 10 mV s^{-1}, $f=83\times2$ Hz and $\Delta E=10$ mV (p-p).

Figure 1 shows that DBA in propiononitrile containing 0.1 M $\mathrm{TBAPF_6}$ (1 M=1 mol dm^{-3}) can be reduced and oxidized at the Pt electrode up to the tetraanion and dication via successive four and two, one-electron transfer steps, respectively. Plots of the peak $\cot\phi$ vs. $\omega^{1/2}$ for the four fundamental harmonic reduction steps at 293, 273, and 253 K were found to behave ideally, yielding linear relationships with ordinary positive slopes ($\phi<45°$), as shown in Fig. 2. A detailed compilation of the rate parameter data in propiononitrile, which resulted from the foregoing treatment procedures, are set out in Table 1. Table 2 presents the results for both the reduction and oxidation of DBA in benzonitrile also containing 0.1 M of $\mathrm{TBAPF_6}$ at both the Pt electrode and HMDE. The data given in Table 2 show the effect of the electrode material on the kinetic parameters of the heterogeneous processes. As Tables 1 and 2 demonstrate, the k_{s} values associated with the different redox couples, except with that of $\mathrm{M^{3-}/M^{4-}}$ at 253

Table 1. Data Obtained for the Electroreduction of DBA in Propiononitrile/0.1 M $\mathrm{TBAPF_6}$ at the Pt Disk Electrode

[M ≡ DBA]

	$\mathrm{M/M^-}$	$\mathrm{M^-/M^{2-}}$	$\mathrm{M^{2-}/M^{3-}}$	$\mathrm{M^{3-}/M^{4-}}$
$-E^{\mathrm{r}}_{1/2}$/V vs. Ag/AgCl	1.364	1.609	2.389	2.752
k_{s}/cm s^{-1}				
293 K	0.253	0.162	0.066	0.052
273 K	0.160	0.106	0.042	0.030
253 K	0.106	0.067	0.024	0.016
α				
293 K	0.50	0.50	0.53	0.50
273 K	0.50	0.50	0.52	0.52
253 K	0.50	0.50	0.50	0.53
ΔG/kJ mol^{-1}	12.77	14.40	15.4	25.10

The values of $10^3 D_0^{1/2}$ at 293, 273, and 253 K are 2.04, 1.7, and 1.54 cm s$^{-1/2}$ respectively.

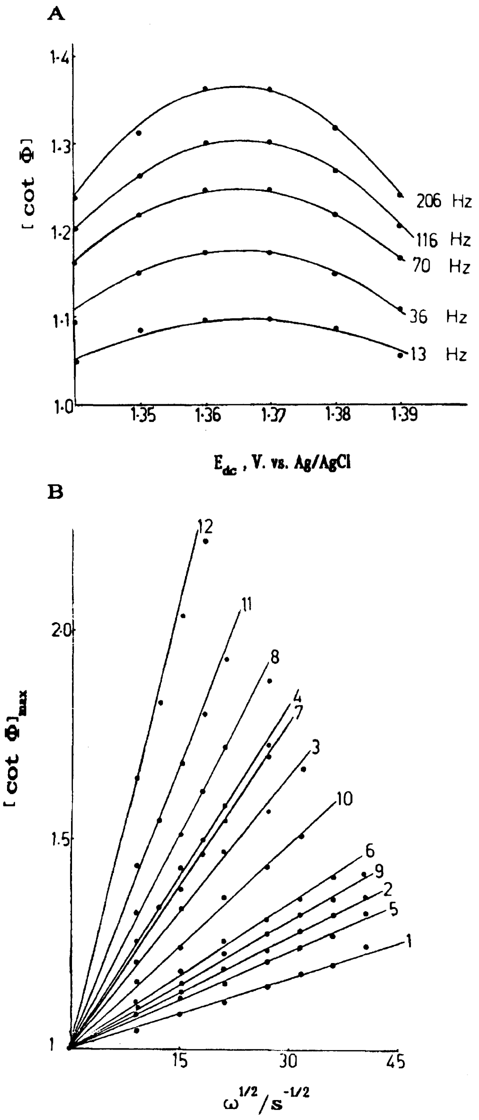

Fig. 2. Experimental results for an ac measurement of DBA in propiononitrile/0.1 M TBAPF$_6$. Conditions as in Fig. 1, $f=8$—330 Hz $\Delta E=10$ mV (p-p). A) $[\cot\phi]_{\max}$ vs. $E_{\rm dc}$ for the first red. step. B) $[\cot\phi]_{\max}$ vs. $\omega^{1/2}$ Curves 1—4 correspond to the formation of the radical, di-, tri-, and tetraanion, respectively, at 293 K; curves 5—8 and 9—12 correspond to the same sequence, but at 273 and 253 K, respectively.

Table 2. Data Obtained for Both the Reduction and Oxidation of DBA in Benzonitrile Containing 0.1 M TBAPF$_6$ at 293 K

[M ≡ DBA]

	$E^{\rm r}_{1/2}$	$k_{\rm s}$/cm s^{-1}		α	
Redox coule	V vs.Ag/AgCl	Pt	HMD	Pt	HMDE
M/M$^-$	−1.370	0.035	0.09	0.53	0.50
M$^-$/M^{2-}	−1.648	0.026	0.09	0.55	0.50
M/M$^+$	0.682	0.042	—	0.52	—
M$^+$/M^{2+}	1.852	0.045	—	0.53	—

$10^3 D_{\rm o}^{1/2}=1.66$ cm s$^{-1/2}$ at 293 K.

K for propiononitrile and benzonitrile, are consistently large, and obviously satisfy the criteria for the nernstian, diffusion-controlled, and charge transfer. They are indicative of the absence of both follow-up chemical reactions and adsorption complications. This is confirmed by the relatively low-energy activation barriers (Table 1), which are characteristic of moderately rapid electrode processes. The given heterogeneous rate constants are the "apparent" $k_{\rm s}$ values uncorrected for double-layer effects.[15,32)]

It is important to note that the heterogeneous rate processes at HMDE are faster than those at the Pt electrode by ≃1.4—2.0 times. α values of exactly 0.5, associated with the DBA reduction at HMDE, compare with those of $0.5+0.03$ for various redox reactions at the Pt electrode, and also reflect the facile nature of the charge transfer at the mercury electrode. Moreover, the relative low activation energies given in Table 1 lead to the conclusion, as expected for a planar or nearly planar organic molecule, that solvent reorganization is the main source of the activation free energy.

This view is further supported by the fact that $\alpha\simeq0.5$, regardless of the apparent $k_{\rm s}$ values and the half-wave potentials associated with the various redox couples. The latter observation is predicted by the Marcus theory[4)] for a solvent reorganization-controlled, heterogeneous, charge-transfer process.

It was observed that acetonitrile has a tendency to form thin films on the platinum electrode which, in turn, leads to marked errors in the determination of the electrode parameters. Therefore, HMDE was used to ensure reproducibility of the measurements. Table 3 provides a list of relevant experimental results obtained for the electroreduction of DBA in acetonitrile/0.1 M TBAPF$_6$. From the values of $k_{\rm s}$, α, and ΔG in the Table, it can be seen that each of the first three redox couples exhibited one facile one-electron transfer process. In both cyclic and ac experiments, the fourth peak, corresponding to the electro-generation of the tetraanion

Table 3. Data Obtained for the Electroreduction of DBA in Acetonitrile Containing 0.1 M TBAPF$_6$ at the HMDE

[M ≡ DBA]

	M/M$^-$	M$^-$/M^{2-}	M^{2-}/M^{3-}	M^{3-}/M^{4-}
$-E^{\rm r}_{1/2}$/V vs.Ag/AgCl	1.328	1.562	2.299	2.640
$k_{\rm s}$/cm s^{-1}				
293 K	0.242	0.242	0.405	—
273 K	0.150	0.150	0.275	—
253 K	0.094	0.094	0.171	—
α				
293 K	0.50	0.50	0.52	—
273 K	0.50	0.50	0.53	—
253 K	0.50	0.52	0.53	—
Δ/G kJ mol^{-1}	14.4	14.4	15.5	—

$10^3 D_{\rm o}^{1/2}=2.16$, 2.00, and 1.86 cm s$^{-1/2}$ at 293, 273, and 253 K, respectively.

species, appeared to be relatively small, with an anodic/cathodic current ratio (i_{pa}/i_{pc}) of $\simeq 0.65$. By the phase-selective second-harmonic response, the two lobes were found to be rather small and unequal.

Under these conditions, in which the charge transfer was complicated by protonation, evaluation of the rate parameters was precluded due to uncertainties associated with measurements of both the phase angle and the reversible half-wave potential.

The most noteworthy aspect of the acetonitrile/TPAPF$_6$ system is that $[\cot\phi]_{max}-\omega^{1/2}$. Profiles for the first three redox couples, at 293, 273, and 253 K, are straight lines passing at unity, but having negative slopes, ($45° < \phi \leq 90°$). This anomalous phase response, however, can be represented by an equation analogous to Eq. 3, but with a negative sign in the front of the second term on the right-hand side of the equation.[17—20]

Subsequent to obtaining α and D, as described before, the apparent k_s value was simply evaluated by equating the negative-slope value of the $[\cot\phi]_{max}-\omega^{1/2}$ profile (Fig. 3) with the negative slope of the equation $-(2D)^{1/2}/2k_s$ (simplified case when α=0.5).

Phase angles exceeding 45°, as observed in this work, were attributed to a negative measured transfer resistance, including a dynamic ψ effect, i.e., repulsion as a result of migration in the electric double layer. Since complications for mass transfer by migration are almost ruled out by the presence of a sufficient amount of the indifferent electrolyte, any interpretation based on the foregoing assumption seems to be unlikely and was not recommended by Sluyters-Rehbbach and Sluyters.[15]

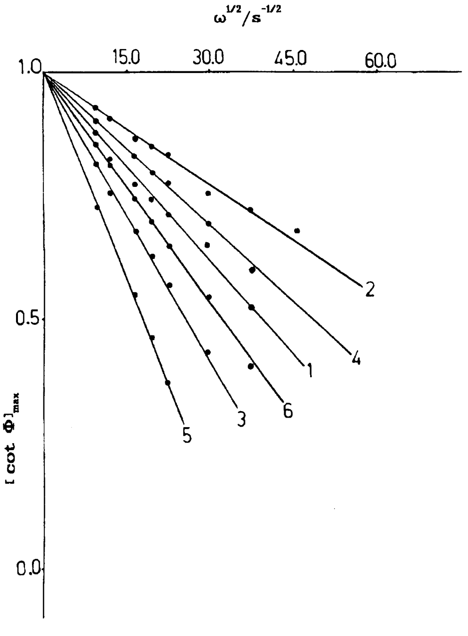

Fig. 3. Frequency dependence of the cotangent of the phase angle for the electroreduction of DBA in acetonitrile/0.1 M TBAPF$_6$ at the THMDE (A= 1.39×10^{-2} cm^2) and f=15—333 Hz.

Temperature	293 K	273 K	253 K
Curve (Red. Step)	1(1st+2nd) 2(3rd)	3(1st+2nd) 4(3rd)	5(1st+2nd) 6(3rd)

Smith[28] pointed out that under appropriate conditions, mechanisms analogous to R1 and R2 are

$$O + n_1e \rightleftharpoons Y \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Z + n_2e \rightleftharpoons R \qquad \text{(R1)}$$

$$\begin{tikzcd} O + n_1e \arrow[r, shift left, rightharpoonup] \arrow[r, shift right, leftharpoondown] & Y + n_2e \arrow[r, shift left, rightharpoonup] \arrow[r, shift right, leftharpoondown] \arrow[l, bend left, "k", leftrightarrow] & R \end{tikzcd} \qquad \text{(R2)}$$

predicted to produce anomalous phase angles,[29—31] where homogeneous chemical and/or catalytic reactions are involved in multi-electron electrode processes. It has therefore been strongly suggested that electrochemical processes coupled with chemical reactions may be a frequent source of abnormal phase angles, as in our case.

The present results concerning the electroreduction of DBA in both propiononitrile and benzonitrile reveal symmetrical negative and positive lobes of the second-harmonic ac response, CV peak-current ratios (i_{pa}/i_{pc}) of approximate unity and linear $\cot\phi-\omega^{1/2}$ profiles for the DBA/TBAPF$_6$ system in both propiononitrile and benzonitrile. These observations demonstrate and quantitatively account for the absence of both follow-up and catalytic chemical reactions, as R1 and R2 predict. Hence, second-harmonic lobes of unequal heights, CV peak-current ratios far less than unity, and nonlinear $[\cot\phi]-\omega^{1/2}$ relations are often obtained in the case of R1 and R2. On the other hand, the reactive tetraanion species ($(DBA)^{4-}$) in acetonitrile probably undergo partial decomposition through a protonation process in a reaction mechanism similar to R2, leading to the formation of less reactive anions, or even the neutral molecule, itself. This assumption may be related with the relatively large $k_{s.3}$ values for the third reduction step, compared with those for the first and second electron transfers, $k_{s.1}$ and $k_{s.2}$ (about two times at all three relevant temperatures, as shown in Table 3). Deviations from linearity usually characterizing $[\cot\phi]_{max}-\omega^{1/2}$ profiles are not evident for the first, second, and third reduction steps, even at low frequencies, as shown in Fig. 3, when homogeneous chemical reactions are coupled to charge-transfer processes. The foregoing interpretation of the phase-angle abnormality thus seems to be less favorable.

In another context Smith explained this anomalous behavior[15,28] by assuming an energy dissipation concept which can be applied to the phase angle[22] through a well-known relation in ac circuit theory,[23]

$$P = E_{dc}I_{dc} + E_{ac}I_{ac}\cos\phi, \qquad (4)$$

where P is the average power dissipation in the ac process; E_{dc} and I_{dc} are the direct potential and current, respectively; E_{ac} and I_{ac} are the amplitude of the alternating potential and current, respectively, and ϕ is the phase angle between the current and potential. Equation 4 indicates that the power dissipation (P positive) corresponds to $-90°\leq\phi\leq 90°$ (ϕ in the first or fourth quadrant), whereas the power gain is realized if ϕ is in the second or third quadrant. Since adsorption of DBA on HMDE in acetonitrile leads to excess surface concentrations, and less freedom for these surface concentrations to be dissipated by the diffusion process, it can be concluded that the over-all mass-transfer process in the presence of absorbed DBA will be more conservative of electrical energy. Equation 4 accordingly suggests that the adsorption of DBA on the electrode surface will increase the phase angle (ϕ), provided that the adsorption rates are not too slow.

The foregoing intuitive argument of Smith was confirmed qualitatively by a number of studies confined to the equilibrium dc potential. Randles and Somerton[24] made observations at Pt-electrode ϕ values larger than 45° in the reduction of *N,N,N′,N′*- tetramethyl-*p*-phenylenediamine. Laitinen and Randles,[25] Randles,[26] as well as Tamamushi and Tanada[27] made similar observations, reporting abnormally larger phase angles.

Finally, it was observed that the cyclic voltammetric, cathodic–anodic peak separation (ΔE) markedly diminishes with decreasing temperature,[7] which is in agreement with the Born model and supports the assumption of enhanced solvation of the species in higher charged states.[33] These findings were further confirmed by the results of this work obtained in the propiononitrile/TBAPF$_6$ system, where both ΔE and the apparent k_s value significantly decrease with decreasing temperature and the successive charging of DBA, respectively. The five times difference between the largest (radical anion formation) and the smallest, (tetraanion formation) k_s values in Table 1 provides clear support in the same direction. On the other hand, the apparent k_s values for the first and second steps in acetonitrile were found to be equal (0.242 cm s^{-1}); in the transition to the trianion formation, it however, increases by about two times (0.405 cm s^{-1}). Such behavior can be ascribed to the adsorption of DBA on the electrode surface, rather than to the enhanced-solvation concept.

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