

Electrochemical Parameters with unusual Alternating Current Phase-Angles

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Abstract : The a.c. technique is employed to evaluate electrochemical characteristics of Naphthalie-1,4,5,8-tetracarboxylic acid bisanilide (NTB). The measurements were carried out in dry and pure propionitrile (PCN) and acetonitrile (CAN) at the hanging mercury drop electrode [HMDE]. An A.C. phase sensitive detector using computer controlled lock-in amplifier was employed. Primary goal of this report, was to establish on a firm the rare behavior of the phase angle associated with a.c. polarograms of the compound. Although, not an initial goal of this study, the electron transfer rate parameters attending the electroreduction of the compound under investigation were determined. This because the results shed some light on the electrokinetics in aprotic solvent which until recently negligible data were available. Experimental Results and comparison of data obtained are reported. The good precision of the method makes it suitable for studying electrochemical data with unusual behavior at electrodes in non aqueous media.

Key words: Naphthalie tetracaboxylic acid bisanilide, Alternating current phase angle, Hanging mercury drop electrode.

1. Introduction

Charge transfer resistance could be negative, and that can produce faradaic admittance of unusual sign. Gerisher and Mehl¹⁾, Schuman²⁾ and Smith and Sobel³⁾ studied theoretically this phenomenon. They have amply demonstrated that coupled homogeneous chemical reactions or even multi charge transfer processes can result in phase angles or faradaic admittance of unusual sign.

The reduction of chlorite ion (ClO_2^-) in 1.0 M NaOH, which was characterized with faradaic admittance of unusual sign, was studied by Gierst *et al.*⁴⁾ They concluded that the two electron transfer step in the reaction mechanism is quasi-reversible in the polarographic sense. On the basis of this finding, the theoretical study of Smith and Sobel would not quite be applicable to their case.

Robert de Levie *et al.*⁵⁾ reported on the Fe (II)-catalyzed reduction of chloride ion solutions. Their results account for the existence of a faradaic admittance with negative in-phase component, while the quadrature one is positive. Also, they indicated that, under optimum (appropriate) conditions, the quasi-reversible reaction of Gierst *et al.*⁴⁾ becomes very fast which is equivalent to the results for the nernstian case given by Smith and Sobel.³⁾ In connection with the same subject, de Levie and Husovsky⁶⁾ reported on the reduction of concentrated Ni(II) solutions where a negative quadrature component and a positive in-phase faradaic admittance have been obtained. Both in-phase and quadrature components are negative were observed and studied by the same authors.⁷⁾

Not very quite recently, Rashwan and Mohran⁸⁾ showed that

the multi-step charge transfer processes of 9,9'-bianthryl-10,10'-dicarbonitrile in acetonitrile in the presence of 0.1 M TBAPF₆ are characterized by phase angles of unusual sign.

Scanning the literature, no electrochemical work have been reported implying naphthaline-1,4,5,8-tetracarbonic acid bisanilide.

It is in connection with the work of our laboratory,⁸⁾ the authors undertook a reexamination of the compound to report on its electrokinetics, especially its observed quite rare unusual alternating current phase angle behavior. In addition, the authors think that there has been considerable interest in the pharmaceutical properties of the molecule.

2. Experimental Procedure

Reagent-grade propionitrile and acetonitrile were further purified and dried according to a previous recommended method.⁹⁾ Tetrabutylammonium hexafluorophosphate (TBAPF₆) obtained from FLUKA was recrystallised twice from pure ethanol and vacuum dried at 120°C.

For sample preparation and purification for electrochemical measurements in superdry media, a type of cell is frequently constructed and described elsewhere.¹⁰⁾ In this cell, three electrodes can be used; the working which is either a platinum disc (Pt) or a Metrohm EA 290 hanging mercury drop electrode [HMDE]. A platinum wire is used as an auxiliary electrode and the reference electrode normally used is an Ag/AgCl where its potential is calibrated for each experiment against the reversible oxidation peak of ferrocene.

An EG&G Princeton Applied Research 5208 Two-Phase Lock-in analyzer is used in conjunction with a computer controlled 273A Potentiostat/Galvanostat to perform funda-

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mental, second harmonic voltammograms (in phase & quadrature signals) and the shift in the phase angle. A positive feedback which is installed inside the 273A is used in all the measurements to minimize the iR-drop effects.

3. Results and Discussion

For detailed description of the equations usually used in determining the parameters of heterogeneous charge transfer processes by applying the A. C. techniques, interested readers are referred to earlier works (for example^{8,11,12}) and the reports cited herein).

The diffusion coefficient, which is required to calculate both the heterogeneous charge transfer rates (k_s -values) and the symmetry factors (α -values) of interest was found to be calculated from the total fundamental harmonic a.c. peak current at $E_{dc} = E_{1/2}$ ¹¹) according to the equation:

$$I_p = n^2 F^2 A \omega^{1/2} D_0^{1/2} C_0^* \Delta E / 4RT.$$

It is found that the foregoing procedure to evaluate the diffusion coefficients instead of the plateau current and the Ilkovic' equation¹³) of the d.c. polarographic measurements gives values without appreciable or significant errors. In fact, both approaches yielded consistent results.

Figure 1 shows the cyclic voltammogram of the electroreduction of 1.3 mM (NTB) at the hanging mercury drop electrode at 273 K. The polarogram consists of well resolved four waves, the fourth of which (the step of tetra-anion formation) is characterized with a large reverse scan which implies that the tetra-anion species of the molecule are readily protonated. The peak-separations values $\Delta E = 54$ and 52, 63 and 70 mV for the first, the second, the third and the fourth wave respectively were found to be consistent with theoretical predictions for nernstian one-electron transfer processes.¹⁴) The unexpected small value obtained for the third step can be ascribed to either a minor protonation of the tri-anion species or probably catalytic effects associated sometimes with multi-charge transfer processes.¹⁵⁻¹⁷) The follow-up chemical

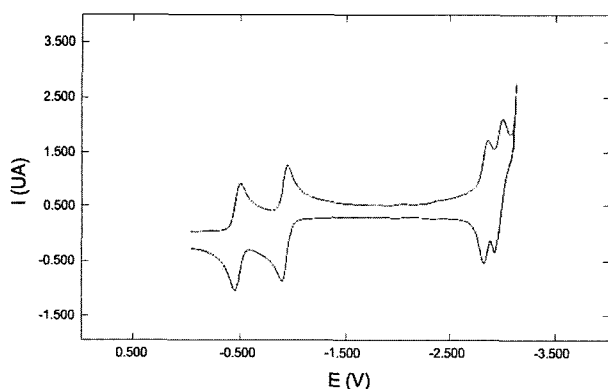


Fig. 1. Cyclic voltammogram of the electroreduction of 0.81 mM of Naphthline-1, 4, 5, 8-tetracarboxylic acid bisanilide (NTB) in propionitrile/0.1 M TBAPF₆ at [HMDE] electrode in 273 K, scan rate = 100 mV/s.

reaction associated with both the third and fourth charge transfer processes make the corresponding half-wave and peak potentials appear positive of the reversible values.¹⁸⁾

In particular, the slow charge transfer rate attending the first step makes the observed half-wave and peak potentials appear negative of the reversible values.¹⁸⁾ Both effects combine to make the measured $E_{1/2}$ -values and ΔE -values considerably smaller than the true reversible value.¹⁸⁾

One aspect of the cyclic voltammogram in Figure 1 which should be noted is the fact that first two peaks are far away separated from the second two steps [$-E_{pc} = 0.624, 1.049, 2.874$ and 3.006 V. vs. Ag/AgCl]. This large potential-separation between the dianion and the trianion polarographic waves attests to large electronic and columbic interactions between the charges as a result of profound π -conjugation between the molecule entities.

Another important point is the disparity between the values of $k_{s,1}$ and $k_{s,2}$, although was not an initial goal of this study. For example, one of the most plausible alternatives involves the idea that the slow rate observed for the reduction of neutral (NTB) is a characteristic of, at least, partially hindered or non-planar molecule. The neutral (NTB) is expected to be non-planar, while the corresponding anion radical (NTB⁻) is planar (or at least nearly so), provided the basis for a rationale of the rate difference associated with the successive charge transfers. Therefore, the first electron transfer to NTB must not proceed through a transition state resembling planar NTB. Consequently, the molecular distortion accompanying this process is considered responsible for the large free energy of activation associated with the anion radical formation. Because such a distortion does not accompany the second, the third or the fourth charge transfers, they are characterized by relatively low activation free energies and hence rapid heterogeneous rates, as one observes with aromatic hydrocarbons.¹⁹⁻²¹⁾

A compilation of the electrochemical parameters calculated through the application of the foregoing treatments are depicted in Table 1.

The experimentally observed values of the peak potential separations do not correspond to the reversible values because of the kinetic complications involved by the follow-up chemical reaction (strictly the protonation process).

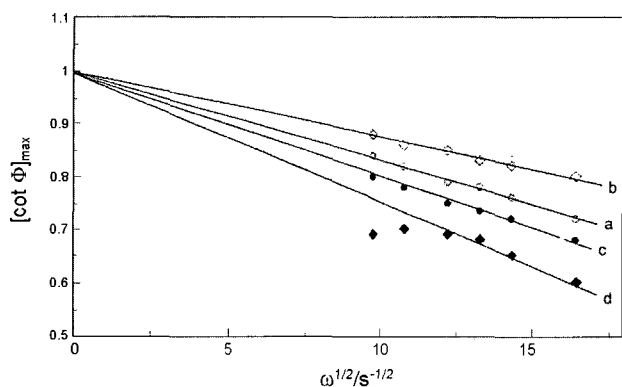
Figure 2 demonstrates the rare behavior for the relation of the cotangent of the phase angle of 0.8 mM NTB in acetonitrile /0.1 M TBAPF₆ with $\omega^{1/2}$ at 273 K on [HMDE]. The negative slopes of the straight lines are taken according to the negative term on the right-hand side of the equation:²²⁻²⁵⁾

$$[\cot \Phi]_{\max} = 1 \pm \{(2\omega D)^{1/2} / k_s [(\alpha/\beta)^{-\alpha} + (\alpha/\beta)^{\beta}]\}.$$

The calculated heterogeneous constants for the two reduction processes (k_s -values) are found to be 0.046 and 0.053 cm/s for the first and the second step respectively. The values are obviously laying at the border between reversible and quasi-reversible behavior (characteristic of moderately fast reactions). It is to be notice that the k_s -values are the apparent data i.e. uncorrected for double-layer effects.^{26, 27}

Table 1. Electrochemical parameters computed from Naphthalene-1, 4, 5, 8-tetracarboxylic acid bisanilide in acetonitrile/0.1 M TBAPF₆ at 273 K on [HMDE].

Redox Couple	NTB/NTB ⁻	NTB ⁻ /NTB ⁻²	NTB ⁻² /NTB ⁻³	NTB ⁻³ /NTB ⁻⁴
-E _{1/2} /V. [vs. Ag/AgCl]	0.610	1.029	2.862	2.980
α-values	0.5	0.5	0.5	0.45
ΔE, mV	54	52	36	70
D ₀ (cm ² /s) × 10 ⁶	0.55	0.55	0.55	0.55
k _s [cm/s] × 10 ³	38	43	34	29

**Fig. 2. Frequency dependence of the cotangent of the phase angle for the electroreduction of 8.10⁻⁴ M NTB in acetonitrile/0.1 M TBAPF₆ at ΔE = 10 mV (p-p) for a.c. amplitude, 273 K and f = 15-43 Hz.**

Curve	a	b	c	d
Red. Step	first	second	third	fourth

Anomalous phase angles can be observed where catalytic reactions are involved in multi-step electrode processes.^{6,22-27)}

Another explanation for the observation of unusual phase angles was given by Sluyters-Rehbach and Sluyters where adsorption of the substrate on the electrode will lead to a concept called energy dissipation.²⁸⁾

However, abnormal phase angles, as observed in this report, can not be attributed to either a negative transfer resistance resulting from migration in the diffuse layer, or to a passivation of the electrode surface. This conclusion is based on the experimental notice that firstly, 0.1 M TBAPF₆ was usually sufficient to prevent migration and secondly, all measurements were carried out at the hanging mercury drop electrode [HMDE] where passivation processes are minimized or absent. A concept strongly confirmed by Sluyters-Rehbach and Sluyters.²⁷⁾

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