Electrochemical study of Hydrogen-Bonding in Anthraquinones.

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Summary: The electrochemistry of five anthraquinones is focused to interpret the intermolecular hydrogen bonding in the presence of four different alcohols, on the basis of their increasing acidity, as proton donors. The quinones were investigated systematically in dichloromethane; acetonitrile and propylene carbonate while the half wave redox potentials were measured through cyclic voltammetry. The hydrogen-bonding power was analyzed from the positive shifts in both the redox waves showing proportional increase with alcohol concentration. The quantitative data was obtained while calculating the thermodynamic association constants and number of alcohol molecules bonded to both anion and dianion of quinones. Both qualitative and quantitative data revealed the quinone-alcohol interaction as hydrogen bonding while strength of hydrogen bond is dependant upon the nature of species involved in this couple. It has been proposed that the basicity of quinone and acidity of the hydroxyl additive both favour the strength of hydrogen bonding.

Introduction

Quinones are potential organic compounds having large number of applications both in biology and chemistry. Quinones for example, serve as an active site of quinoenzymes in biological systems. They also act as coupler of electron and proton transfer in energy transducing membranes for respiration and photosynthesis [1-4]. Their biological action is often linked to their electron transfer rates and redox potentials [5]. The reduction products of quinones are essentially a radical anion ($Q^{\cdot-}$) and dianion (Q^{2-}), the former is also known as semiquinone [6]. In this regard the study of kinetics, equilibrium chemistry of coupled electron and proton transfer reactions has given much information about the molecular structure [7-9]. Apart from this the environmental factors which regulate the potentials and reaction pathways have been studied as well [10, 11].

Hydrogen-bonding is well recognized and is an important aspect of these compounds in biological functions [12, 13]. It was found that hydrogen-bonding interactions between quinones and proteins in biological systems are responsible for adjusting the redox potentials of the quinones [14]. It is also reported that hydrogen-bonding provides information about molecular recognition, regulation of bond strength and structural backbone in molecular assemblies [15]. More interestingly the hydrogen-bonding strength can be controlled by the electrochemistry of receptors, i.e. quinones [16]. In recent years hydrogen-bonding of 1, 4-benzoquinone, radical anion and dianion have been studied extensively to understand the structure function relationships [17-20]. The fascinating behaviour of quinones in absence and presence of different proton sources is a continued investigation [21-24].

It has been established that the voltammetric behaviour of quinone is strongly affected by the nature of substituents and surrounding environmental conditions [25-27]. Three important series of quinones namely Benzoquinones (BQs), Naphthoquinones (NQs) and Anthraquinones (AQs) have potential applications in chemistry as well as in biology as reported above. The data, describing hydrogen-bonding, so far reported is about few derivatives of one type of series or other, mostly it is about BQs and NQs [28-33, 25]. Quite a little attention is given to AQs from this point of view [26]. AQs have been recognized for anti-inflammatory, analgesic and tissue repairing properties [34]. In the recent past AQs were discussed in terms of their anticancer properties [35].

Keeping in view the above novel applications five AQs were subjected to electrochemical studies for qualitative and quantitative information. The change in the shape of resulting voltammograms is used to discuss the qualitative behaviour. On the other hand single global association model is used to quantify the hydrogen bonding interaction. Recently

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Ignacio Gonzalez and co-workers presented a new model for the characterization of hydrogen bonding in quinones [23]. The model is based upon the concept that the association between donor protons and quinones takes place through successive equilibria. Further these equilibria depend upon the concentration of hydrogen bond donor. Although the new model has its own significance and precision but involves a lot of practical work (at least three sets with 30 pairs of experimental data points for each additive-quinone couple) and rigorous calculations. On the other hand single global equilibrium model is simple in both aspects. Additionally the explanations based upon the new approach are still applicable rather beneficial to explain the results obtained by single global equilibrium model.

In the present work an attempt is made to study the hydrogen-bonding systematically in three different solvents, namely dichloromethane (DCM), acetonitrile (AN) and propylene carbonate (PC), with increasing solvent polarity. The alcohols used were ter-butylalcohol (t-butanol); 2-propanol, ethanol (EtOH) and methanol (MeOH) with increasing acidity order (See table1). The association between alcohols and quinones has been treated in terms of single global association equilibrium constants ($\beta_{eq}(1)$ and $\beta_{eq}(2)$) and number of alcohol molecules (n and m) bonded with anion and dianion of quinones respectively. Discussion has been extended to electrochemical characteristics of bonded quinones in different media. Similar data on some BQs and NQs have already been submitted elsewhere.

Table-1: pK_a values of the alcohols.

Alcohols	$pK_a(H_2O)$
Ter-butylalcohol	19.0
2-Propanol	17.1
Ethanol	15.9
Methanol	15.5

Results and Discussion

Qualitative study

In dry neutral aprotic solvents the anthraquinones studied showed two cathodic and two anodic waves. The two waves correspond to sequential formation of the semiquinone ($Q^{\cdot-}$) and dianion (Q^{2-}) of respective quinone. From the peak potentials the half wave reduction potentials were calculated as given in Table-2. The results are in agreement with reported values having reproducibility of ±0.005V [36].

Table-2: Half wave reduction potential values of the anthraquinones vs. SCE for first and second wave in different solvents at 25 ± 0.1C°.

Quinone	$-E_{1/2}^{(1)}$/V			$-E_{1/2}^{(2)}$/V		
	DCM	AN	PC	DCM	AN	PC
DHAQ	0.570	0.580	0.600	0.890	0.970	0.910
DAcAQ	0.620	0.680	0.700	1.020	1.110	1.070
AQ	0.860	0.900	0.840	1.220	1.300	1.220
AAQ	0.960	1.020	0.950	1.320	1.420	1.310
DAAQ	1.100	1.180	1.120	1.400	1.550	1.430

The uncertainty in '$E_{1/2}$' values is ± 0.005V.

Cyclic voltammograms obtained, in the absence of alcohols, showed quasireversible behaviour for most of the compounds in three solvents. DHAQ and DAcAQ showed nearly reversible behaviour in AN while AQ, AAQ and DAAQ depicted irreversibility for second redox wave in PC. On adding the alcohols a positive shift was observed in both the waves. The shift observed in first reduction peak is negligible but quite significant in second reduction peak. The positive shift increases smoothly with increase in concentration of additive without disturbing symmetry of the voltammogram. The AQs used (Fig. 1) have the following increasing Lewis basicity strength on the basis of the substituents attached, DHAQ < DAcAQ < AQ < AAQ < DAAQ. Representative cyclic voltammograms of some AQs are given in Fig. 2. The relative acidic strength of alcohols is given in Table-1 from which it is clear that acidity increases from t-butanol to methanol [28].

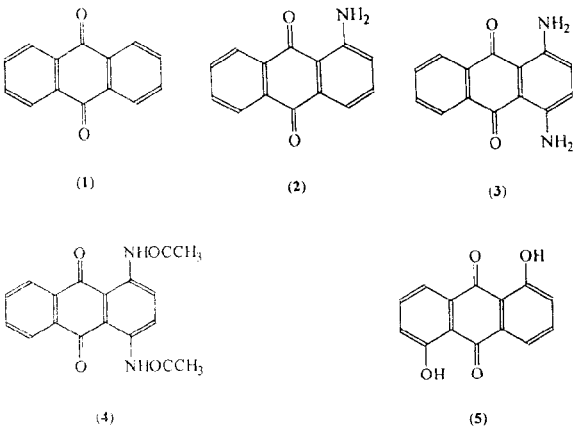

Fig. 1: Structural formulae of the anthraquinones used.(1) 9,10-Anthraquinone (AQ), (2) 1-Amino-9,10-anthraquinone (AAQ) (3)1,4-Diamino-9,10-anthraquinone (DAAQ), (4), 1,4-Diacetamido-9,10-anthraquinone (DAcAQ) and (5) 1,5-Dihydroxy-9,10-anthraquinone (DHAQ).

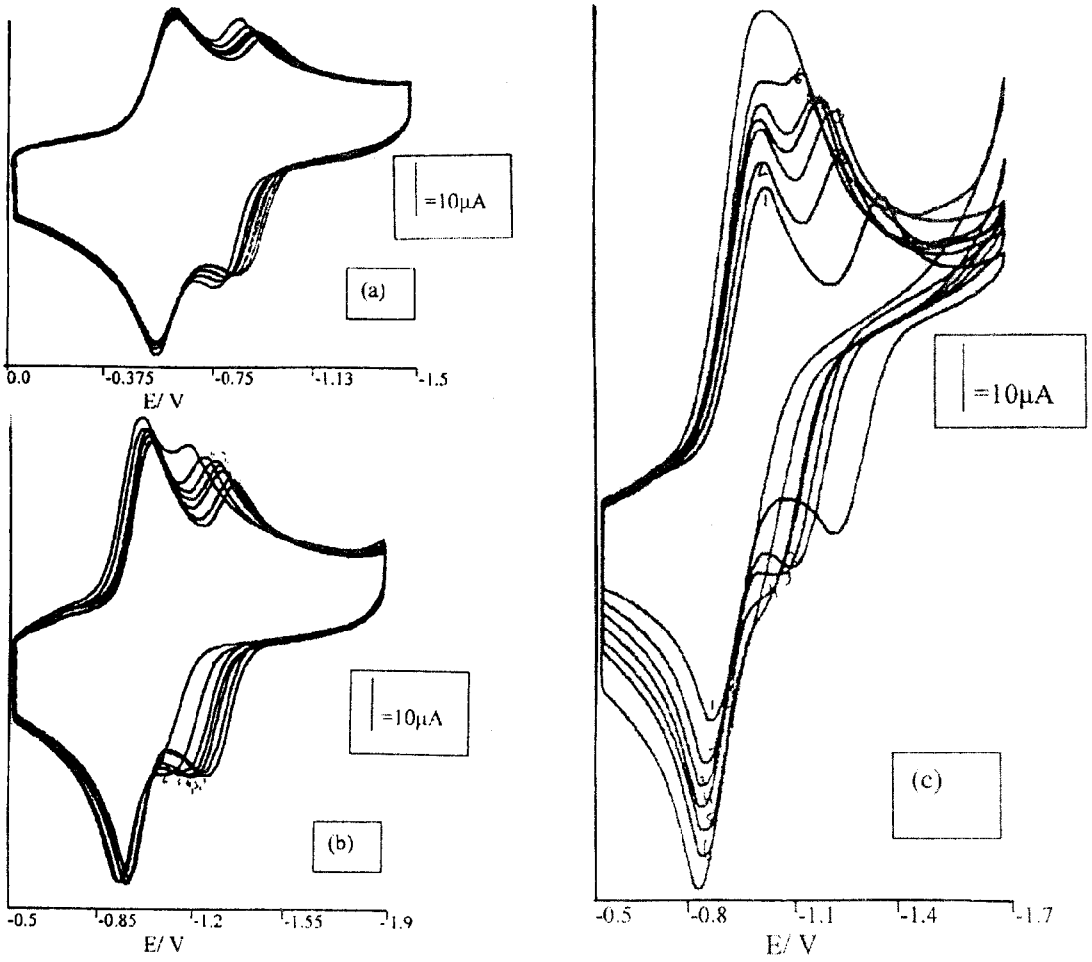

Fig. 2: Cyclic voltammograms of (a) DHAQ in AN (b) AAQ in AN (c) AAQ in DCM with increasing concentrations of MeOH, [0.0, to 1.5 M], from right to left (1 to 6) in figure, at $0.1Vs^{-1}$ using GC working electrode vs. SCE.

In case of semiquinone-alcohol interaction the maximum positive shift was less than 50mV between MeOH (the strongest hydrogen bonding power additive) and DAAQ (the strongest hydrogen bonding power host). A systematic decrease in positive shift is followed by other four compounds with MeOH according to decreasing trend of their basicity. In DHAQ and DAcAQ the electron withdrawing nature of hydroxyl and acetaamido groups decreased the basicity of respective quinone hence a small anodic shift was observed. On the other hand unsubstituted AQ and its amino derivatives are more basic because of intrinsic basicity and electron donating nature of NH_2 group respectively. Consequently a large anodic shifting was observed for the same concentration of hydroxyl additive. Fig. 2 depicts the relative effect between DHAQ (less basic quinone) and AAQ (more basic quinone) on addition of MeOH in AN. The shift produced by EtOH is nearly of the same order as that of MeOH and is logical because of comparable pK_a values of two alcohols. The other two additives being less acidic produced even a small rather negligible anodic shift as expected.

For a given alcohol concentration the shift produced was much larger for the second reduction step as compared to first step. The magnitude of this shift ranged from 50 mV to 250 mV and in some cases to such an extent that second wave was merged with the first one. This is very much obvious from the

causative high pKa value of the dianion of respective AQ to low pKa value of the anion radical. As the quinone basicity increased from DHAQ to DAAQ the corresponding magnitude of positive shift also increased.

A further explanation of relative strong hydrogen bonding in NH_2-quinones can be given in comparison to DHAQ, as a less interacting member. In hydroxy-quinone the –OH group causes intramolecular hydrogen bonding when hydrogen of attached hydroxyl group interacts with carbonyl oxygen, as reported previously for hydroxy substituted quinones [37]. This type of intramolecular hydrogen bonding produces a hindrance and disfavours the intermolecular hydrogen bonding between incoming alcohol and the host quinone leading to a small positive shift. Apparently it looks that β-NH_2 quinone may have such type of intramolecular hydrogen bonding but the present results are contrary to this hypothesis. This apparent anomaly is attributed to the fact that the lone pair of nitrogen in amino group is displaced towards the oxygen of quinone making the latter more basic and thus more susceptible for strong intermolecular hydrogen bonding.

The effects of less acidic alcohols (t-butanol and iso-propanol) are different only in magnitude of positive shift but similar qualitatively. This will be further enlightened in quantitative data of hydrogen bonding. As reported earlier this shift is not because of solvent polarity but ascribed to specific alcohol-quinone interaction [28]. Note that the acidity constant of alcohols will be further low (large pK_a values) in aprotic solvents with the decrease in dielectric constant value from water to DCM via PC and AN. This large difference in pK_a values of alcohols and reduced quinone products excludes the possibility of protonation even if there is a change in peak height of first reduction wave. This specific interaction is nothing but hydrogen-bonding which increases with increasing basicity of quinones.

Quantitative treatment of Intermolecular Hydrogen Bonding Interaction

For quantitative treatment of intermolecular hydrogen bonding interaction the following reaction scheme is adopted as given by previous workers [28, 39].

$$Q + e \leftrightarrow Q^{\cdot-}$$

$$Q^{\cdot-} + n\,(\text{alcohol}) \leftrightarrow Q^{\cdot-}(\text{alcohol})_n$$

$$Q^{\cdot-}(\text{alcohol})_n + e \leftrightarrow Q^{2-}(\text{alcohol})_n$$

$$Q^{2-}(\text{alcohol})_n + (m\text{-}n)\text{alcohol} \leftrightarrow Q^{2-}(\text{alcohol})_m$$

Peover and Davis have interpreted these reactions in terms of cation anion association equilibrium [38]. By analogy with their treatment and as proposed by Gupta and Linschitz [28] the equation for first reduction step becomes

$$E_{1/2} = E_{1/2}^{\circ} + (RT/F)\ln(1 + K_{eq}^{(1)}[\text{alcohol}]^n) \qquad (1)$$

Where $E_{1/2}^{\circ}$ is the half wave potential in absence of alcohol and $K_{eq}^{(1)}$ is the equilibrium constant for first reduction step in the presence of alcohol. The above equation can be written as

$$\Delta E_{1/2} = n(RT/F)\ln[\text{alcohol}] + (RT/F)\ln K_{eq}^{(1)} \qquad (2)$$

If $K_{eq}^{(1)}[\text{alcohol}] >> 1$ then a plot of $\Delta E_{1/2}$ vs. log[alcohol] should give a straight line with slope 2.3nRT/F, from which the value of n can be estimated. The equilibrium constant for the first reduction step can be estimated from intercept or rearranging equation 1 to obtain

$$\exp(f\Delta E_{1/2}) = 1 + K_{eq}^{(1)}[\text{alcohol}]^n \qquad (3)$$

Where $f = F/RT$, $\Delta E_{1/2} = E_{1/2} - E_{1/2}^{\circ}$.

Using the same analogy for hydrogen bonding equilibrium of second reduction step we have.

$$\exp(f\Delta E_{1/2}) = (1 + K_{eq}^{(2)}[\text{alcohol}]^m) / (1 + K_{eq}^{(1)}[\text{alcohol}]^n) \qquad (4)$$

Where m and $K_{eq}^{(2)}$ are the number of molecules of alcohols hydrogen bonded to Q^{2-} and the corresponding equilibrium constant respectively. For strong hydrogen bonding neglecting "1" in numerator and denominator we can write

$$\Delta E_{1/2} = 1/f \ln(K_{eq}^{(2)}/K_{eq}^{(1)}) + (m\text{-}n)\ln[\text{alcohol}] \qquad (5)$$

Taking n from the first reduction step values of m can be obtained by plotting $\Delta E_{1/2}$ vs. log

[alcohol]. Having established n and m and $K_{eq}^{(1)}$, $K_{eq}^{(2)}$ can be calculated from intercept of plot or directly from equation 4.

From Table-3 it is evident that $K_{eq}^{(1)}$ and 'n' were obtained only for more basic quinones. The values for these thermodynamic parameters for a given quinone are changed according to the acidity of added alcohol. The relative magnitude of association constant values is in favour of the rational given before for the hydrogen bonding interaction while considering the anodic shifting in the two waves. Trend of this sort may be attributed to the inductive and steric effect of the substituents attached. $K_{eq}^{(1)}$ values are higher for quinones with e-donating substituents as compared to those with e-withdrawing substituents.

The strong anodic shift in second wave because of intermolecular hydrogen bonding is manifested well from large values of $K_{eq}^{(2)}$. It is evident from the tabulated data (table 3) that the association constant value increases with the increase in the basicity of quinone as does $K_{eq}^{(1)}$. The only difference is that the values of m and $K_{eq}^{(2)}$ are quite

Table-3:Electrochemical parameters for hydrogen-bonding of anthraquinones in presence of alcohols.

Quinone	alcohol	solvent	n	$K_{eq}^{(1)}$	m	$K_{eq}^{(2)}$
DHAQ	t-butanol	AN	c	c	0.65	8.6
	2-propanol	AN	c	c	1.60	20
	EtOH	AN	c	c	1.9	82
	MeOH	AN	c	c	2.0	1.2×10^2
	MeOH	DCM	c	c	2.5	1.1×10^3
	MeOH	PC	c	c	1.8	1.2×10^2
DAcAQ	t-butanol	AN	c	c	0.83	11
	2-propanol	AN	c	c	1.0	19
	EtOH	AN	c	c	1.2	1.2×10^2
	MeOH	AN	0.80	5.0	3.2	3.9×10^2
	MeOH	DCM	c	c	2.7	1.3×10^3
	MeOH	PC	c	c	2.3	2.3×10^2
AQ	t-butanol	AN	c	c	0.83	13
	2-propanol	AN	c	c	1.1	65
	EtOH	AN	c	c	2.4	4.1×10^2
	MeOH	AN	0.80	5.0	2.9	2.5×10^3
	MeOH	DCM	0.40	3.3	2.5	4.4×10^4
	MeOH	PC	c	c	2.4	2.6×10^2
AAQ	t-butanol	AN	c	c	1.1	23
	2-propanol	AN	c	c	2.3	7.2×10^2
	EtOH	AN	0.61	4.8	3.2	3.2×10^3
	MeOH	AN	0.60	3.7	2.8	6.7×10^2
	MeOH	DCM	c	c	3.8	2.4×10^4
	MeOH	PC	c	c	2.6	2.1×10^2
DAAQ	t-butanol	AN	c	c	1.1	61
	2-propanol	AN	0.50	4.3	3.0	5.2×10^3
	EtOH	AN	1.1	19.5	4.5	1.9×10^5
	MeOH	AN	1.1	12	4.2	1.8×10^5
	MeOH	DCM	1.0	10	6.0	5.0×10^6
	MeOH	PC	c	c	5.8	2.0×10^4

Units of $K_{eq}^{(1)} = M^{-n}$ and $K_{eq}^{(2)} = M^{-m}$. c = Potential shifts are very small to calculate n and $Keq^{(1)}$.

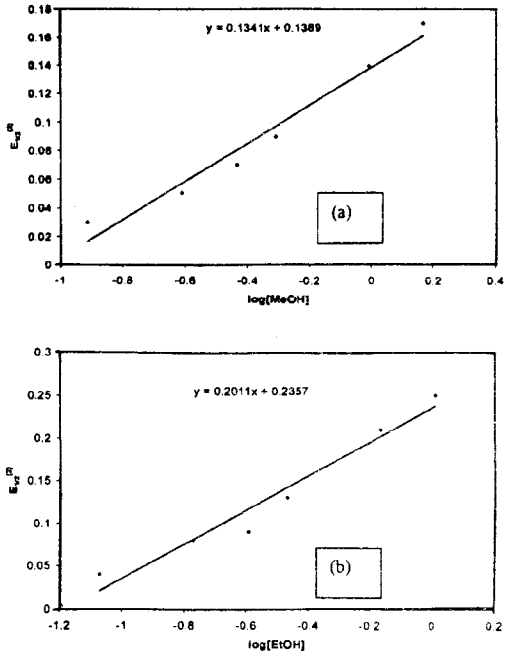

Fig. 3: (a): Plot of $\Delta E_{1/2}^{(2)}$ vs. log [MeOH] for DAcAQ in PC. (b): Plot of $\Delta E_{1/2}^{(2)}$ vs. log [EtOH] for DAAQ.

large as compared to n and $K_{eq}^{(1)}$ respectively. The values of $K_{eq}^{(2)}$ confirm the strong interaction of Q^{2-}--[alcohol] couple and are in good agreement with the positive shift behaviour in cyclic voltammograms as conferred above. The above discussion is further supported by the plots of $\Delta E_{1/2}$ vs. log [alcohol] as given in Fig. 3

Solvent Effect

Some of the properties of the solvents used are given in table 6. It was observed that the values of n, m, $K_{eq}^{(1)}$and $K_{eq}^{(2)}$ are higher in DCM followed by AN and lowest in PC. The solvent effect can be discussed for two aspects, as a proof for the existence of hydrogen bonding instead of protonation and relative effect in hydrogen bonding.

In general solvent polarity favours the protonation over hydrogen-bonding [39]. This is very much true in present case where the hydrogen bonding is high in presence of least polar solvent, DCM. It was also observed that PC being more polar and viscous suppressed the peak heights and deleted the second oxidation peaks in more basic quinones. The relative polarity difference in AN and PC

Table-4: Properties of the solvents used.

Solvent	ϵ	η/cp	d /g(mL)$^{-1}$
DCM	8.93	0.44	1.326
AN	37.5	0.38	0.782
PC	64.9	2.4	1.201

ϵ = dielectric constant, η = viscosity, d = density

demands much strong hydrogen bonding in AN which was not found so. This behaviour can be rationalized in terms of solvent viscosity and density (see Table-4). The PC is most viscous solvent having comparable density value to that of DCM relative to AN. Therefore it is suggested that a viscous and denser solvent may provide better environment for weak intermolecular hydrogen bonding especially after the attachment has begun. This can be further investigated by trying more solvents.

Experimental

Chemicals

9,10-Anthraquinone (AQ) (98 % -Merck) was of best available grade and used as such. 1-Amino-9,10-anthraquinone (AAQ) (98 %), 1,4-Diamino-9,10-anthraquinone (DAAQ) (98 %), 1,5-Dihydroxy-9,10-anthraquinone (DHAQ) (98 %), 1,4-Diacetamido-9,10-anthraquinone (DAcAQ) (98 %) were gifted by (Prof. Hajdu from California state university) USA. Tetrabutylammonium fluoroborate ($TBABF_4$) (FISHER Scientific Company) of electrochemical grade was used as supporting electrolyte. Dichloromethane (DCM) (99.5 % -Fluka), Acetonitrile (AN) (99.7 %, HPLC grade, Merck) and Propylene Carbonate (PC) (99 %, BDH Chemicals) were dried over molecular sieves before use. Pure ferrocene (>99 % -BDH Chemicals) was used as such. The alcohols used are; t-Butanol (99 % -Merck), 2-Propanol (>99 %Fluka), Ethanol (99.5 % Merck) and Methanol (99.5 % Merck). All chemicals were used as received without further purification unless specified.

Instrumentation

Cyclic Voltammetry (CV) was performed with three electrode system consisting of glassy carbon (GC, 3mm^2) working electrode, saturated calomel reference electrode (SCE) and a platinum wire (0.5mm^2 dia.) counter electrode. Princeton Applied Research (PAR) Electrochemical System 370 coupled with X-Y recorder VP-65423A was used as CV measuring device. Temperature was maintained using thermostat (LAUDA model K-4R).

Procedure

All measurements were made using ferrocene as internal indicator at 25 ± 0.1^{0}C. The solutions were purged with argon gas to provide oxygen free atmosphere and was passed over the solutions during the measurements. Quinones used were of 1mM concentrations with 0.1M supporting electrolyte. The alcohols were added incrementally to the solution using a micropipette with a concentration range 0.05 M to 1.4 M.

Conclusions

The anthraquinones studied showed quasireversible behaviour in the three solvents but irreversible pattern was observed for more basic quinones in PC. Addition of alcohols (proton donors) with such low concentrations caused a systematic positive shift in the redox waves of the quinones. This shift is attributed to specific interaction, hydrogen-bonding, between anions and dianions of quinones with the concentration of added alcohols. The resulting anodic shift was very small in the first wave but significantly large in the second wave. This depicts the weak interaction of semiquinone-alcohol interaction in comparison to strong dianion-alcohol interaction for the same concentration of alcohol. Hydrogen-bonding interaction was found to be increased with the increasing basicity of quinones. The increased acidity (small pKa values) of alcohols also favoured this interaction. Quantitative analysis was made in terms of electrochemically obtained hydrogen-bonding parameters, n, m and K_{eq}. It was found that these values are in good agreement with the positive shifting observed in cyclic voltammograms in a given quinone-alcohol couple.

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