The Visible Absorbance Maximum of 2-Hydroxy-1,4-naphthoquinone as a Novel Probe for the Hydrogen Bond Donor Abilities of Solvents and Solvent Mixtures

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Summary. The electronic absorption spectra of 2-hydroxy-1,4-naphthoquinone (HNQ) in one- and two-component solvents are discussed. The visible absorption of this reagent has been shown to arise from a charge-transfer transition of the zwitterionic tautomer stabilized by a hydrogen bond donating solvent. The formation constant of the 1:1 hydrogen bonded complex with methanol, ethanol, and n-propanol has been determined at 25 °C from the spectral behaviour in mixed solvents. The tautomerization equilibrium of HNQ in aqueous ethanol is demonstrated and characterized. The dependence of the absorbance maximum of HNQ on the hydrogen bond donor ability of the solvent in the visible spectrum, as measured by the *Taft-Kamlet* α parameter, has been established. Experimentally derived evidence is supplied to justify the recommendation of HNQ as a novel probe for hydrogen bond donor ability in pure solvents and in mixed aqueous solvents.

Keywords. 2-Hydroxy-1,4-naphthoquinone; Absorption spectra; Hydrogen bond donor abilities of solvents; Tautomeric equilibria.

Das Absorptionsmaximum von 2-Hydroxy-1,4-naphthochinon im sichtbaren Bereich als neues Maß für die Wasserstoffbrückenbindungsbildungsfähigkeit von Lösungsmitteln und Lösungsmittelgemischen

Zusammenfassung. Die Absorptionsspektren von 2-Hydroxy-1,4-naphthochinon (HNQ) in Ein- und Zweikomponentensystemen werden diskutiert. Die Absorption im sichtbaren Bereich stammt von einem *charge-transfer* – Übergang des zwitterionischen Tautomers, das über Wasserstoffbrückenbindungen zum Lösungsmittel stabilisiert wird. Die Bildungskonstanten der binären Komplexe mit Methanol, Ethanol und n-Propanol wurden aus spektroskopischen Daten in Lösungsmittelgemischen bei 25 °C emittelt. Das Tautomeriegleichgewicht von HNQ in wäßrigem Ethanol wird diskutiert. Die Abhängigkeit des Absorptionsmaximums von HNQ von der Wasserstoffbrückenbindungsbildungsfähigkeit des Lösungsmittels wird mittels des *Taft-Kamlet* – Parameters α beschrieben. Experimentelle Ergebnisse ermutigen zur Verwendung von HNQ als neue Testsubstanz für die Wasserstoffbrückenbindungsbildungsfähigkeit von reinen und gemischten Lösungsmitteln.

Introduction

It has been recognized that the effect of hydrogen bonding on the electronic spectra of organic compounds is useful in several aspects. The hydrogen bond donor (HBD)

ability, or nearly equivalently, the electron pair acceptance ability, of solvents has been studied by the use of several probes. The most commonly used index that is more or less specific for this quantity is the *Kamlet-Taft* parameter α [1]. Some other solvatochromic indices, such as E_T [2], Z [3], or AN [4], were reported as more general solvent polarity indices, but are sensitive to the solvent HBD ability to a fairly good extent and related linearly to α and π^* (Index of solvent polarity/polarizability, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect [5, 6].

Probe solutes that had been used to evaluate HBD properties by means of UV/visible solvatochromic indicators [7, 8] all show dependences on some solvent properties other than α (mainly π^* [9] and in some cases β (solvent's ability to accept a proton in a solute-to-solvent hydrogen bond)). Therefore, a solely α dependent probe is advantageous.

In the present investigation, valuable information is derived from the electronic spectra of 2-hydroxy-1,4-naphthoquinone, *HNQ*, in various solvent systems. The solvatochromic response of this reagent in HBD media is clarified. The study is extended to selected mixed-solvent systems including nonpolar-HBD pairs and water-solvent mixtures. The potentialities of *HNQ* for the prediction of the HBD properties of the solvents prompted us to explore further its unique behaviour. The visible spectrum of *HNQ* is recorded over the entire composition ranges in aqueousacetone, acetonitrile, N,N-dimethylformamide, dimethylsulfoxide, dioxane, methanol, and ethanol. The solvent dependent function of *HNQ*, which has not been hitherto explored, is the adequate dependence of the visible absorbance maximum on the hydrogen bond formation tendency, α, for pure solvents and mixed aqueous solvents.

We believe that this is the first documented example of a prediction of a zwitterionic tautomer which is solvent stabilized to measure the HBD abilities of the solvent system. As a novel probe for HBD properties, *HNQ* offers clear advantages over many of the solvatochromic indicators, being sensitive to α alone and not to β or π^*.

Results and Discussion

The absorption spectra of *HNQ* in non aqueous solvents are shown in Fig. 1. The figure covers the visible region of the spectrum in which there appears one absorption band depending on the hydrogen bond donation properties of the solvent. The spectra of this compound indicate that the band intensity is influenced by the nature of the solvent. The linear variation of absorbance with solute concentration denotes that association of solute molecules, especially in dilute solutions, does not occur. The absorption band below 250 nm is assigned to a $\pi \rightarrow \pi^*$ transition within the benzenoid system, whereas the bands near 270 and 330 nm correspond to the $\pi \rightarrow \pi^*$ transitions of the quinonoid system. The long wavelength band at ~ 450 nm can be assigned to intramolecular charge transfer from the substituent to the naphthoquinone nucleus.

The visible spectra of *HNQ* in various mixed aqueous solvents are examined and the solution spectra for some representative solvent systems are shown in Figs. 2a–d. An equilibrium between two species of *HNQ* is responsible for the spectral changes
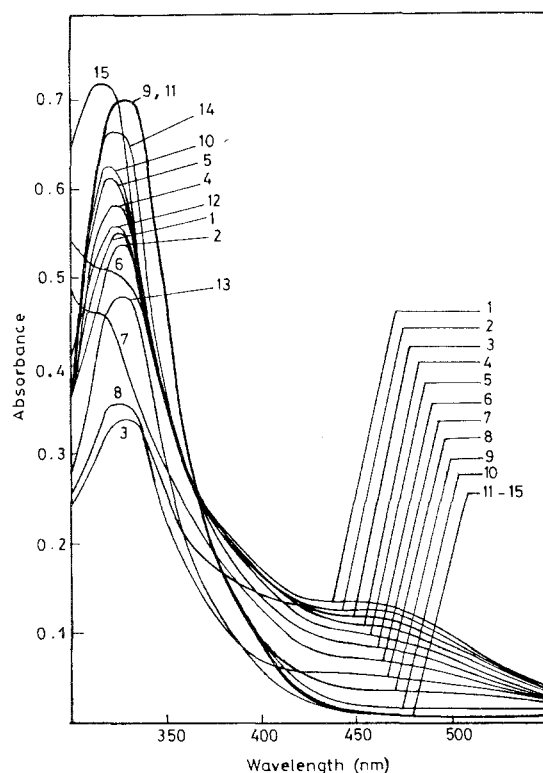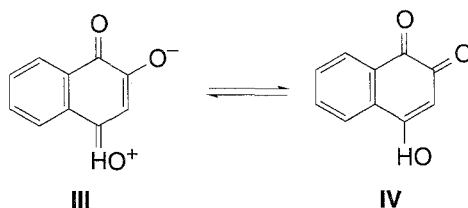
Fig. 1. Absorption spectra of $2 \times 10^{-4} M$ HNQ in 1) methanol, 2) ethylene glycol, 3) ethanol, 4) n-propanol, 5) iso-propanol, 6) N,N-dimethylformamide, 7) dimethylsulfoxide, 8) acetonitrile, 9) chloroform, 10) acetone, 11) dichloromethane, 12) carbon tetrachloride, 13) cyclohexane, 14) ethylacetate, 15) dioxane

observed. The existence of an ill-defined isosbestic point is due to the frequency shift and to a slight change of the band shape as solvent composition is varied.

It is clear from the pattern of the spectra of HNQ that this compound exists in two tautomeric forms: the molecular form (**I**) and the zwitterionic form (**II**).
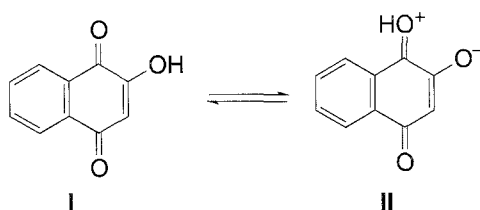
The only possible zwitterionic structure is shown as **II**, the alternative **III** is merely a resonance form of **IV**. The latter is in fact a possibility for one of the species present, though an unlikely one, since *ortho*-quinonoide forms are always heavily disfavoured.
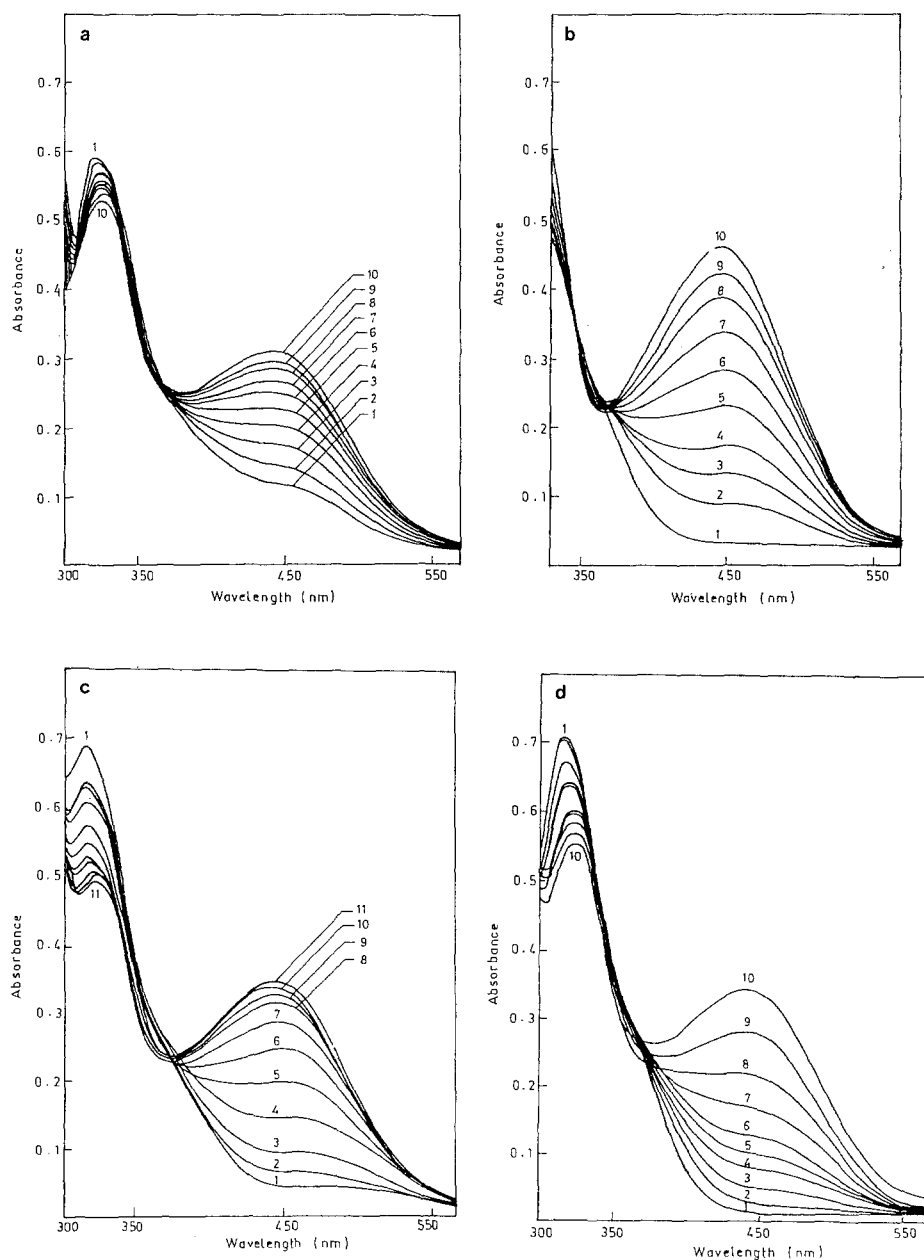
Fig. 2. a. Absorption spectra of $2 \times 10^{-4} M$ HNQ in aqueous methanol; volume fraction of water: 1) zero, 2) 0.1, 3) 0.2, 4) 0.3, 5) 0.4, 6) 0.5, 7) 0.6, 8) 0.7, 9) 0.8, 10) 0.9; **b.** absorption spectra of $2 \times 10^{-4} M$ HNQ in aqueous acetone; volume fraction of water: 1) zero, 2) 0.1, 3) 0.2, 4) 0.3, 5) 0.4, 6) 0.5, 7) 0.6, 8) 0.7, 9) 0.8, 10) 0.9; **c.** absorption spectra of $2 \times 10^{-4} M$ HNQ in aqueous dimethylsulfoxide; volume fraction of water: 1) zero, 2) 0.1, 3) 0.15, 4) 0.2, 5) 0.3, 6) 0.4, 7) 0.5, 8) 0.6, 9) 0.7, 10) 0.8, 11) 0.9; **d.** absorption spectra of $2 \times 10^{-4} M$ HNQ in aqueous dioxane; volume fraction of water: 1) zero, 2) 0.1, 3) 0.2, 4) 0.3, 5) 0.4, 6) 0.5, 7) 0.6, 8) 0.7, 9) 0.8, 10) 0.9

The neutral molecule **I** is expected to predominate in non polar solvents, whereas the zwitterion **II** should become more prevalent in hydrogen bonding donor HBD solvents.

The absence of an absorption band of $\lambda_{max} \sim 450\,nm$ in non polar or polar aprotic solvents is due to the predominance of the neutral form of HNQ in these solvents. The HBD solvents, such as water and alcohols, will tend to stabilize the zwitterion more than the neutral molecule. Therefore, in non polar or protophilic aprotic solvents (such as $DMSO$), the neutral form of HNQ will predominate, and as the hydrogen bond donor ability of the solvent increases, the absorption at 450 nm increases and the equilibrium will be shifted toward the zwitterionic species.

The appearance of the band at $\sim 450\,nm$ in hydroxylated solvents is interpreted on the base that these solvents would stabilize the zwitterionic species through intermolecular hydrogen bonding and formation of a solvent-to-solute molecular complex in which the solvent, but not the solute, is the hydrogen bond donor.
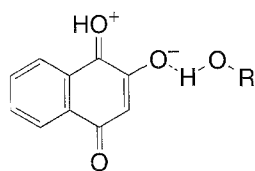
In this case, the total solvent effect shows a dependenc on the solvent hydrogen bonding donor parameter α [1] which provides a measure of the solvent ability to donate a proton in a solvent-to-solute hydrogen bond.

As shown in Fig. 2, the visible absorption of HNQ undergoes a blue shift as solvent polarity is increased. This behaviour may be interpreted on the basis that the solute dipole decreases during the transition. The promotion of an electron from an orbital would give rise to a large change in the solute dipole. The large molar absorptivity, the blue shift observed when solvent polarity is increased, and the disappearance of the band in non polar or non-HBD solvents suggest that the low-energy absorption band in HNQ is due to a charge-transfer transition in the zwitterionic form of the molecule rather than an $n \rightarrow \pi^*$ transition. The rapid decrease in the intensity of the maximal absorption of the c.t. band as the HBD properties of the solvent decrease can be ascribed to the decrease in the concentration of the solvent-to-solute molecular complex. Thus, the c.t. band at 450 nm becomes less intense as the equilibrium is shifted toward the neutral form by lowering the HBD ability of the solvent. The latter brings about noticeable changes both in frequency and intensity of the transition.

In HBD solvents, HNQ exhibits two bands which do not have direct analogies in the spectrum of 1,4-naphthoquinone. A band at $\sim 270\,nm$, on the longer wavelength side of 240 nm band, appears most prominently in the spectra of the cationic and anionic species. It is assumed that this absorption arises largely from charge transfer from the oxygen atom to the naphthoquinone moiety. This interpretation is consistent with the observation that the band shows a red shift upon either protonation of the ring or ionization of the hydroxyl group. This is because either process lowers the energy required for the transition. The second band not having an analogy in 1,4-naphthoquinone is the band at 450 nm which has been identified as being a charge-transfer transition in the zwitterionic form of the molecule. On the

basis of the above discussion, it is reasonable to expect such a transition to occur even at lower energies because both protonation of the quinonoid oxygen and ionization of the hydroxyl group have occurred in the zwitterion.

Spectral behaviour of HNQ in mixed solvents and molecular complex formation

The formation of solvent-to-solute molecular complexes of *HNQ* with HBD solvents was investigated by studying the spectral changes of this reagent in mixed solvents. A set of absorption spectra was measured taking the three component system which consists of *HNQ*, the HBD solvent, and an inert solvent. The concentration of the HBD component was varied in steps from 1.33 *M* to 13.31 *M*. As shown in Figs. 3a–c, the spectra of *HNQ* in mixed solvents show a regular increase in the c.t. band maxima as the solvent composition is enriched in the HBD component. The increase of the absorption can be ascribed to the increased participation of the hydrogen-bonded complex in the equilibrium mixture. The spectral changes in mixed solvents give rise to well-defined isosbestic points at ∼370 nm which denote the solution equilibrium between hydrogen-bonded complex and free species.

As can be seen from Figs. 2d and 3c, the spectral behaviour in dioxane-water and dioxane-alchohol solvent systems are analogous. The increased proportion of the HBD solvent in each system causes a gradual increase in the absorption at 450 nm. For each binary solvent system, the data near the c.t. band maxima are consistent with the existence of a single 1:1 hydrogen-bonded complex species. It is worth mentioning that the similar spectral changes in acetone-water and dioxane-water solvent systems (Figs. 2b, d) can be considered as convincing evidence for molecular complex formation wherein the zwitterionic form of *HNQ* is bonded to a water molecule, the solvent of the high HBD ability. The presence of an as low as 0.025 mole fraction of water in the above solvent mixtures leads to the appearance of the absorption at ∼450 nm which increases progressively as the solvent system is enriched in water. In pure acetone, a low basic aprotic solvent, *HNQ* exists predominantly in its neutral form. Thus, the reagent can be used for the colorimetric detection of low concentrations of water in mixed aqueous acetone.

The changes of the c.t. band maxima in different mixed aqueous solvents reflect the variation of the organic cosolvent in stabilizing the neutral form of *HNQ*. The pronounced stabilization of zwitterionic form in aqueous solvent mixtures is due to the great tendency of water molecules, as compared with other solvents, to donate hydrogen.

The formation constant (K_f) of 1:1 *HNQ* – HBD solvent molecular complex is determined from the spectral behaviour in mixed solvents using the following methods:

Method 1 [10]:

$$1/(\varepsilon - \varepsilon_f) = [1/K_f(\varepsilon_b - \varepsilon_f)](1/c_{alc}) + [1/\varepsilon_b - \varepsilon_f] \qquad 1$$

In equation 1, ε_f and ε_b are the molar extinction coefficients of free and H-bonded molecules, respectively, and ε is that of a solution in which the alcohol concentration
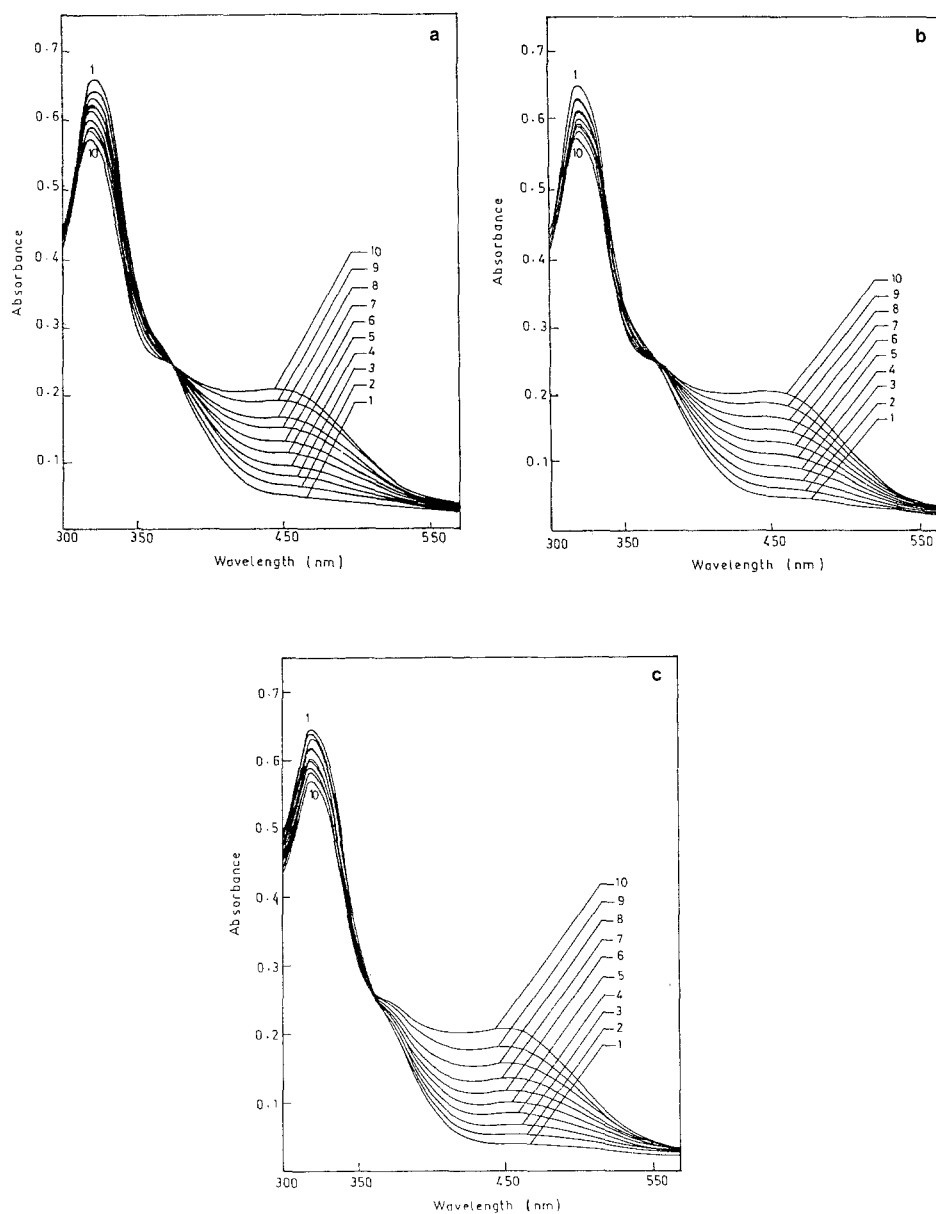
Fig. 3. a. Absorption spectra of $3 \times 10^{-4} M$ HNQ in n-propanol–carbon tetrachloride; $c_{\mathrm{alc}} = 1$) 1.33 M, 2) 2.66 M, 3) 3.99 M, 4) 5.32 M, 5) 6.65 M, 6) 7.98 M, 7) 9.32 M, 8) 10.65 M, 9) 11.98 M, 10) 13.31 M; **b.** absorption spectra of $3 \times 10^{-4} M$ HNQ in n-propanol–cyclohexane; $c_{\mathrm{alc}} = 1$) 1.33 M, 2) 2.66 M, 3) 3.99 M, 4) 5.32 M, 5) 6.65 M, 6) 7.98 M, 7) 9.32 M, 8) 10.65 M, 9) 11.98 M, 10) 13.31 M; **c.** absorption spectra of 3×10^{-4} $M HNQ$ in n-propanol–dioxane; $c_{\mathrm{alc}} = 1$) 1.33 M, 2) 2.66 M, 3) 3.99 M, 4) 4.32 M, 5) 6.65 M, 6) 7.98 M, 7) 9.32 M, 8) 10.65 M, 9) 11.98 M, 10) 13.31 M

c_{alc}. All extinction cofficients refer to a given wavelength. On extrapolating the linear plot of $1/\varepsilon - \varepsilon_f$ vs. $1/c_{alc}$ to the point where $1/\varepsilon - \varepsilon_f = 0$, K_f was obtained as $K_f = -1/c_{alc}$.

Method 2 [11]:

$$\log(A - A_0)/(A_{max} - A) = n \log c_{alc} - \log K_f \qquad 2$$

A, A_0, and A_{max} are the absorbances in mixed, inert, and HBD solvents, respectively. The plot of $\log(A - A_0)/(A_{max} - A)$ vs. $\log c_{alc}$ is linear with a slope n, the number of HBD – solvent molecules of about unity. $\log K_f$ is equal to value of $\log c_{alc}$ at which $\log(A - A_0)/(A_{max} - A) = 0$.

Method 3 [12]:

$$(A_1 - A_0)/A_0 c_{alc} = K_f \varepsilon_1/\varepsilon_0 - K_f A_1/A_0 \qquad 3$$

A_1 and A_0 are the absorbances at a given wavelength in mixed and inert solvents, respectively, and ε_0 and ε_1 are molar extinction coefficients of the solute and complex species. According to equation 3, the plot of $(A_1 - A_0)/A_0 c_{alc}$ against A_1/A_0 should be linear with a slope of K_f and an intercept at $K_f \varepsilon_1/\varepsilon_0$.

The mean values of K_f for *HNQ* – methanol, ethanol, and *n*-propanol molecular complexes in cyclohexane or carbon tetrachloride as solvents are given in Table 1. For each binary solvent system, the data near the c.t. band maximum are consistent with the existence of a single 1:1 *HNQ*–HBD solvent complex. The constancy of K_f values for a given binary system at different wavelengths supports the existence of a 1:1 complex in solution [13].

On detailed examination of the spectral behaviour of *HNQ* in mixed aqueous solvents at different *pH* values [14], it becomes evident that the general ionization scheme of this compound can be represented as given below.
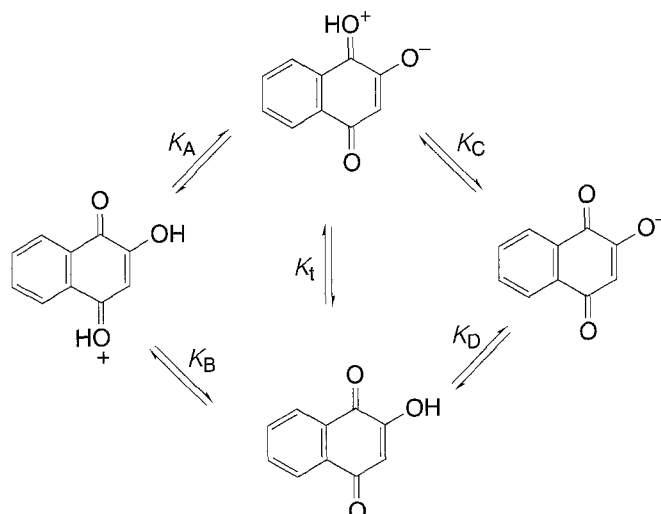
Table 1. Average values of K_f ($l \cdot mol^{-1}$) and ΔG ($kcal \cdot mol^{-1}$) for HNQ-alcohol complexes at 25 °C

System	K_f	$-\Delta G$
Methanol-cyclohexane	98.54 ± 0.4	2.72
Methanol-CCl$_4$	83.32 ± 0.2	2.62
Ethanol-cyclohexane	74.35 ± 0.2	2.55
Ethanol-CCl$_4$	62.50 ± 03	2.45
n-propanol-cyclohexane	28.23 ± 0.4	1.98
n-propanol-CCl$_4$	22.50 ± 0.6	1.84

The true ionization constants for the dipolar (K_A and K_C) and non charged (K_B and K_D) forms are related to the experimentally determined ionization constants K_{a1} and K_{a2} by equations 4–6:

$$K_{a1} = K_A + K_B \qquad 4$$

$$1/K_{a2} = 1/K_C + 1/K_D \qquad 5$$

Thus:

$$K_t = K_A/K_B = K_D/K_C \qquad 6$$

By assuming that the value of pK_B is the same as that of the pK_a of 2-methyl-1,4-naphthoquinone (MeNQ), the tautomeric equilibrium constant (K_t) and the values of all dissociation constants in the above scheme can be calculated (equations 7–10, [15, 16].)

$$K_t = K_{a1}/K_B - 1 \qquad 7$$

$$K_t = antilog(pK_{MeNQ} - pK_{a1}) - 1 \qquad 8$$

$$1/K_t = K_C/K_{a2} - 1 \qquad 9$$

$$1/K_t = antilog(pK_{a2} - pK_{MeNQ}) - 1 \qquad 10$$

The above calculations were performed to allow the tautomeric equilibria of HNQ in solutions to be studied. The values of the constant K_A, K_B, K_C, and K_D for the tautomeric forms of HNQ in water-ethanol medium containing 23.5 mol% ethanol at 25 °C are given in Table 2.

Table 2. Tautomeric and acid dissociation constants of the cationic, neutral, and zwitterionic forms of HNQ ($I = 0.1 \, mol \cdot l^{-1}$ (NaClO$_4$), 25 °C $\pm$ 0.1, 23.5 mol% ethanol)

K_t	K_A	K_B	K_C	K_D
2.388	2.501×10^{-4}	1.047×10^{-4}	9.373×10^{-6}	2.238×10^{-5}

Hydrogen bond donation properties of organic solvents and mixed aqueous
solvents as probed by the visible spectrum of HNQ

It has been shown elsewhere [17] how the solvatochromic indices α, π^*, and β can be applied to unravel, quantify, and rationalize solvent effects on many types of
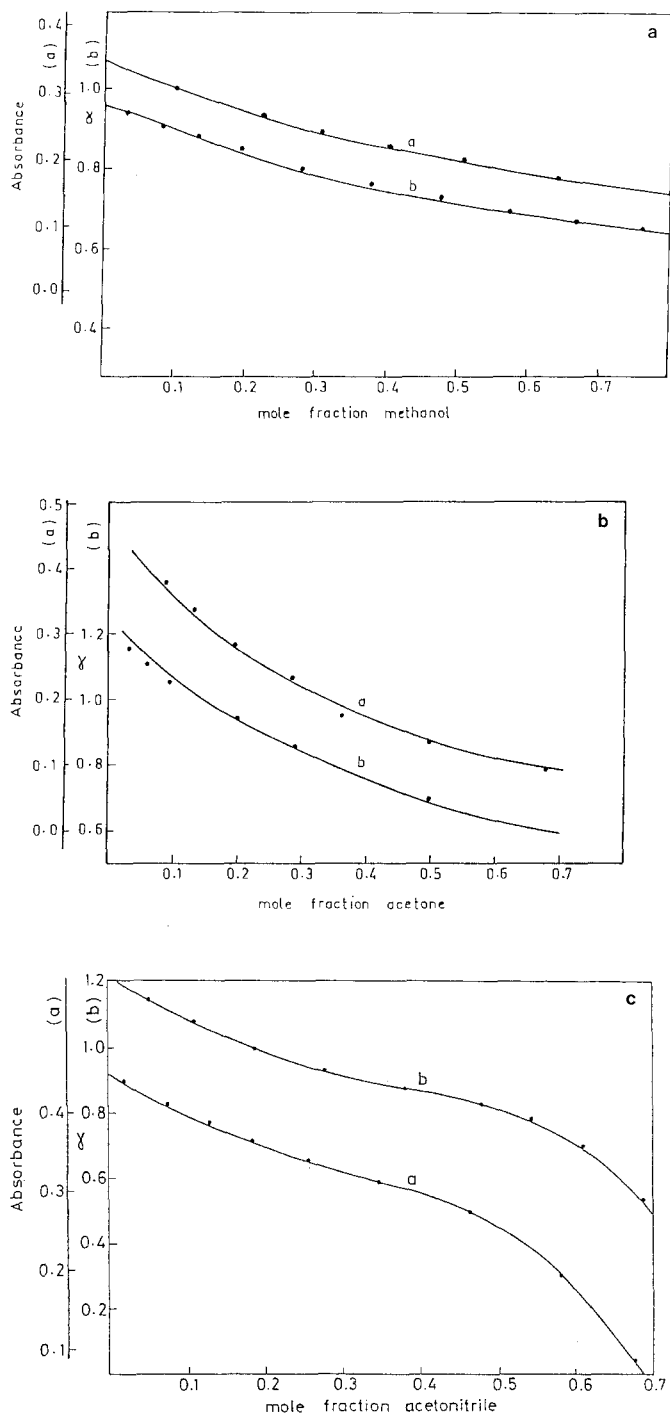

Fig. 4. a. Absorbance values of $2 \times 10^{-4} M$ HNQ in aqueous methanol (curve a); values of α obtained from Ref. [21] (curve b), plotted against the mole fraction of methanol; **b.** absorbance values of $2 \times 10^{-4} M$ HNQ in aqueous acetone (curve a); values of α obtained from Ref. [21] (curve b), plotted against the mole fraction of acetone; **c.** absorbance values of $2 \times 10^{-4} M$ HNQ in aqueous acetonitrile (cyrve a); values of α obtained from Ref. [21] (curve b); plotted against the mole fraction of acetonitrile

physicochemical properties. The multiparameter system of *Kamlet, Abboud*, and *Taft* used to analyze solvent effects on many free energy proportional properties was formulated in a schematic equation of the form

$$XYZ = XYZ_0 + s(\pi^* + d\delta) + a\alpha + b\beta \qquad 11$$

where XYZ is any solvent dependent property of the probe solute, XYZ_0 is the regression value in cyclohexane for that property, and δ is a polarizability correction term [17, 18]. The above generalized equation may be reduced to a more manageable form by judicious choice of solvents and indicators. The $s\pi^*$, $d\delta$, $a\alpha$, or the $b\beta$ term, or any combination of them, may equal zero. Correlations involving different combinations of the above parameters and various types of reactivity parameters and physicochemical properties have been established [17].

When solvents (but not solutes) are hydrogen bond donors, the multiple solvent dependencies on π^* and the solvent HBD acidity parameter α are expressed in equation 12.

$$XYZ = XYZ_0 + s(\pi^* + d\delta) + a\alpha \qquad 12$$

As far as the solvent HBD ability is concerned, it is of importance in this connection to find probes that are considerably more sensitive to α than to, say, π^*. Most of the probe solutes used for the evaluation of HBD properties show dependencies on some solvent properties other than α, so that having a solely α dependent probe is advantageous. This is particularly useful for solvent mixtures where values of π^* are unavailable.

In this work, an attempt is given to relate the changes of the c.t. band maxima of *HNQ* to the HBD ability of the solvent. There is a good linearity between the intensity of maximal absorption (at fixed concentration of the solute) and the Z value of the HBD solvents, used as well as α as a solvatochromic parameter. Also, the band intensity is found to vary linearly with the peturbation energy (ΔE_{HB}) of *Figures* [19] which measures the influence of HBD solvents.

The substantial agreement between the HBD ability of neat solvents and the intensity of the maximal absorption of *HNQ* encouraged us to examine other solvent systems that can fulfill this function. We studied the visible spectral changes of *HNQ* over the entire solvent mole fraction range in different mixed aqueous solvents. The
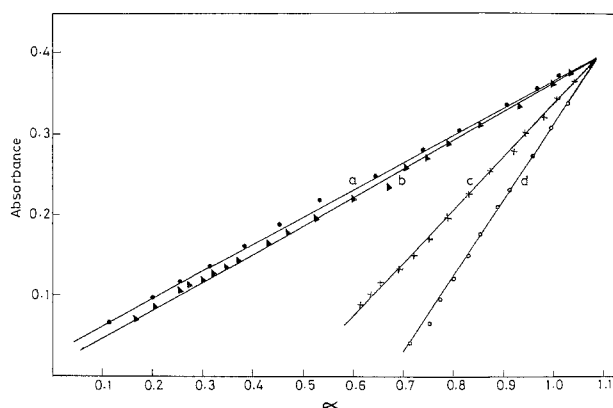

Fig. 5. Variation of the absorbance maximum of HNQ $(2 \times 10^{-4} M)$ with α for water – aprotic solvent mixtures; co-solvent: a) dimethylsulfoxide, b) dimethylformamide, c) acetone, d) acetonitrile

cosolvents used include acetone, acetonitrile, N,N-dimethylformamide, dimethylsul-
foxide, dioxane, methanol, and ethanol. The absorbance vs. mole fraction curves for
all mixtures investigated show a striking resemblance to the corresponding plots of
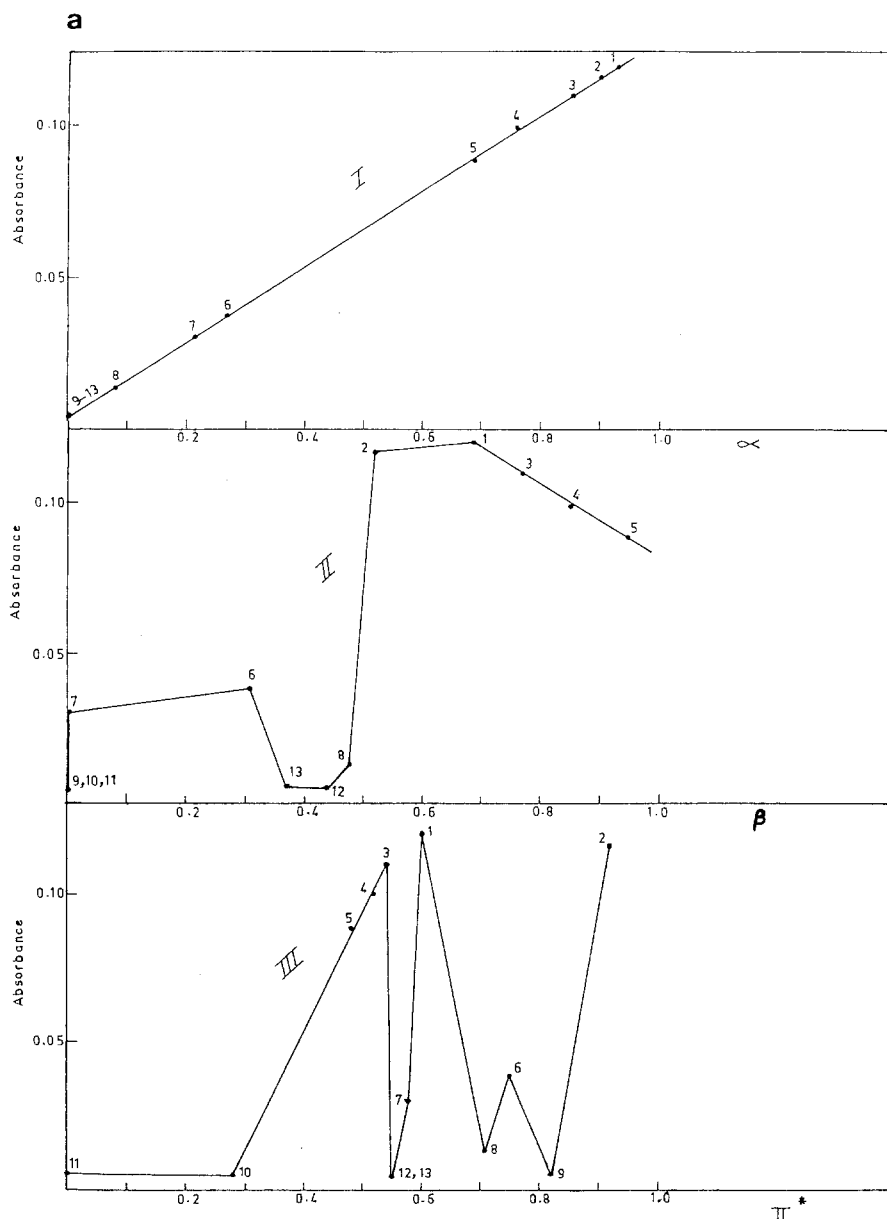α vs. mole fraction of the organic cosolvent [20, 21] (cf. Fig. 4). The values of α for

Fig. 6. a. Variation of the absorbance maximum of HNQ ($2 \times 10^{-4} M$) with solvatoahromic param-
eters α (I), β (II), and π^* (III) for pure solvents; 1) methanol, 2) ethylene gycol, 3) ethanol, 4) n-
propanol, 5) iso-propanol, 6) acetonitrile, 7) chloroform, 8) acetone, 9) dichloromethane, 10) carbon
tetrachloride, 11) cyclohexane, 12) ethylacetate, 13) dioxane; **b.** variation of the absorbance maximum of
HNQ ($2 \times 10^{-4} M$) with β and π^* for mixed aqueous solvents; I, II mixed aqueous acetone, III, IV
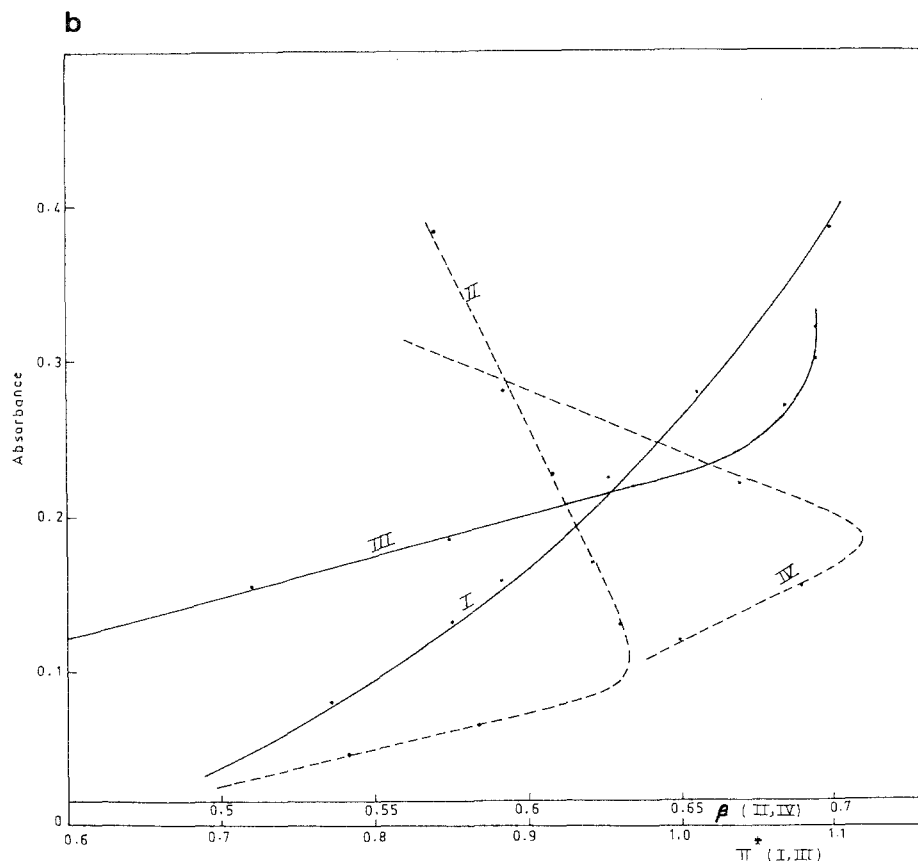mixed aqueous methanol

b

Fig. 6. *(Continued)*

water-solvent mixtures were taken from the literature [20–22] whenever possible. The non-HBD solvents show a gradual decrease of absorbance with increasing solvent mole fraction. This behaviour is similar to that observed previously for the variation of α with solvent composition.

The curve of absorbance *vs.* the mole fraction of acetonitrile has a characteristic S-shape. This shape has already previously been noted in the plot of α against solvent composition [23]; this reflects a parallelism between the c.t. band maxima of HNQ and the α value for aqueous acetonitrile.

The linearity of absorbance *vs.* α plots for the water–aprotic solvent mixtures investigated (*cf.* Fig. 5) indicates a substantial agreement of the visible maximal absorption of HNQ and α. As shown in Figs. 6a and 6b, HNQ is advantageous over many of the other probes in its sensitivity to α alone and not to β or π^*.

The results obtained in this work led us to conclude that the intensity of the maximal absorption in the visible spectrum of HNQ can be used as an indicator for the hydrogen bonding donation properties of organic solvents and water–aprotic solvent mixtures. Examination of the reliability and limitation of the data for HNQ when applied to multiple regression as a predictive function for α are in progress.

It is noteworthy in this connection that the values of the formation constant (K_f) of the 1:1 hydrogen-bonded complex of HNQ in cyclohexane as a solvent were found to vary linearly with the α value of the HBD solvent. As a conclusion, HNQ is unambiguous in its response to solvent HBD properties, and its zwitterionic structure allows only hydrogen bond acceptor behaviour toward HBD solvents.

Experimental

All solvents used in the present work were of spectroscopic reagent quality and were purified by standard methods just prior to the preparation of the solutions of HNQ for spectral measurements. 2-Hydroxy-1,4-naphthoquinone (HNQ) was obtained from Aldrich and purified by recrystallization. Concentrations of the reagent were $5 \times 10^{-4}-10^{-6}\,mol \cdot l^{-1}$. Water-solvent mixtures were prepared by weight and doubly distilled water was used throughout. The absorption spectra were recorded on a Perkin-Elmer model Lambda 3B UV Vis spectrophotometer using 10 mm matched quartz cells. Ionization constants of HNQ in water-ethanol solutions were determined using a procedure given elsewhere [16].

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