SHORT PAPER

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Solvation and temperature effects on the proton transfer equilibria between 2,5-dihydroxy-*p*-benzoquinone and amines†

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Solvation and temperature effects on the proton transfer equilibrium constant K_{PT} between 2,5-dihydroxy-*p*-benzoquinone (DHBQ) and some aliphatic and aromatic amines have been investigated spectrophotometrically by using UV-Vis spectroscopy.

Keywords: 2,5-dihydroxy-p-benziquinone, amins

Introduction

A number of benzoquinones have been recognised as biological electron carriers. They function as one and two gates during the primary reactions of photosynthesis and in the respiratory chain of mitochondria.[1–5]

The proton transfer (PT) is an essential step in many biological processes.[6–8] The behaviour of particular systems depends on the shape of the potential for the PT which very strongly depends on the environment. In previous papers the solvent and temperature effects upon the PT process were studied.[9–11] The solvation effect on a reaction is either long or short range in nature. The long range effect is the result of solvent polarity and may be described by such units as the dielectric constant or Taft's π scale, which relates to the ease with which charge separation may occur in solution.[12]

The short-range effect results from direct interaction between solute and solvent molecules with the formation of hydrogen bonds. It is expressed in such units as Taft's α or β values.[13–15] The UV-Vis spectroscopy seemed to be a suitable method for study of PT process in H- bonded complexes.[9–12]

Proton transfer equilibria including hydroxybenzoquinones and proton acceptors are not reported in the literature. Hence the aim of the present work was to study the proton transfer equilibria between DHBQ and a group of tertiary aromatic and aliphatic amines by applying UV-Vis spectroscopy.

An important aim of this work was the study of the solvation effect on the PT equilibria between DHBQ and various aminopyridines and triethylamine (TEA) which should give more information about the structure of the hydrogen bonded complexes in the presence of proton acceptor solvents.

Another aim of this work was the determination of the thermodynamic data of the proton transfer complex formation between DHBQ and the investigated amines which should give more information about the strength and the steric hindrance of the formed PT complexes.

Experimental

2,5-dihydroxy-*p*-benzoquione, the solvents and the amines were of spectroscopic grade. The spectra were recorded on a Shimadzu 160-A UV-Vis recording spectrophotometer employing 1-cm matched silica cells in the wavelength range 200–800 nm. The temperature was adjusted to an accuracy of ± 0.05°C by using a TB-85 thermobath. Solutions of DHBQ (5×10^{-3} M) and the different concentrations of the investigated amines were prepared immediately before measurement and thermostated at the desired temperature. 2-ml aliquots from the mixture were transferred into a well thermostated chamber containing the UV cell.

Methods of calculation

The proton transfer equilibrium constant with a reproducibility of 3% was computed utilising the minimum–maximum absorbances method.[16–20] In this method the equilibrium constants were estimated from the absorbances at the proton transfer analytical band at different amine concentrations using the following equation

$$A_{maximum} = A_{mixture} + \frac{A_{mixture} - A_{minimum}}{K_{PT}\, C_{amine}}$$

and the set of equilibrium constants were averaged. The thermodynamic parameters were calculated as described previously.[10,11]

Results and discussion

The pK_a valves of DHBQ were determined potentiometrically. It has been found that DHBQ is a dibasic acid with pK_1 = 4.59 and pK_2 =8.77. The acid exists in three forms, the neutral yellow H_2A at very low low pH and in non polar solvent. In 1,4-dioxane this form exhibits two absorption bands at 280 and 380 nm in the UV spectrum attributed to the π–π* transition of the quinonoid ring and the proton transfer complex between DHBQ and dioxane respectively. The dark red A^{2-} stable at high pH and the orange HA^- in polar solvents such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The form HA^- exhibits two absorption bands in the UV-Vis spectrum at 288 and 500 nm attributed to the π–π* transition of the quinonoid ring and the form HA^- respectively.

The hydrogen bonding interaction between DHBQ and a series of aromatic and aliphatic tertiary amines in 1,4-dioxane was studied utilising UV-Vis spectroscopy. It has been found that dioxane is displaced by the amines and hence the band at 380 nm shifts bathochromically. Since the form HA^- exhibits a band at 500 nm, the range 380–500 nm can be used to study the 1:1 proton transfer equilibrium between DHBQ and the investigated amines.

Figure 1 represents examples of the electronic spectra of the hydrogen bonding interaction between DHBQ and aromatic and the aliphatic tertiary amines. These amines are 2,4,6-trimethylpyridine Fig. 1a, tri-*n*-butylamine, Fig. 1b and triethylamine Fig. 1c. As seen in Fig. 1, with gradual increase

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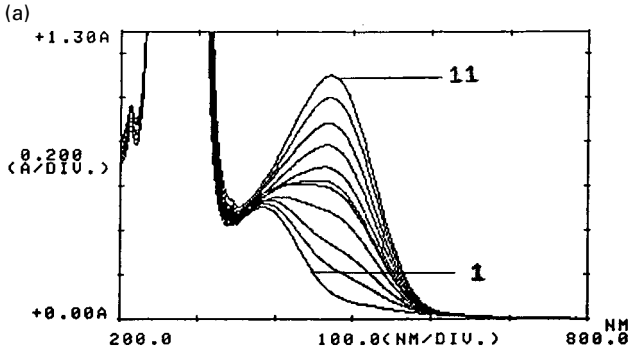


Fig. 1a Absorption spectra of 5×10^{-3} M DHBQ in 1,4 dioxan in presence of various concentrations of 2,4,6 trimethylpyridine: (1) 0,0; (2) .0375; (3) 0.075l (4) 0.15; (5) 0.187; (6) 0.225; (7) 0.3; (8) 0.37; (9) 0.45; (10) 0.6; and (11) 0.75 M.

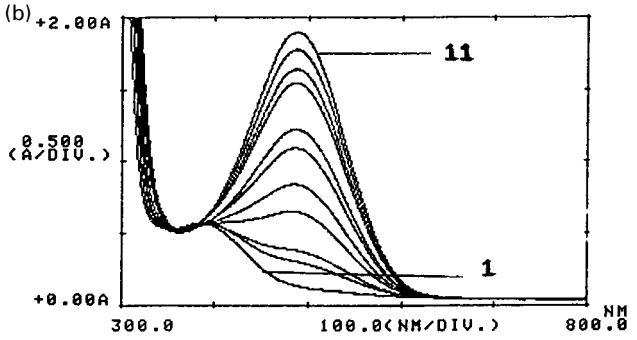


Fig. 1b Absorption spectra of 5×10^{-3} M DHBQ in 1,4 dioxan in presence of various concentrations of Tri-*n*-butylamine: (1) 0,0; (2) $1{,}55 \times 10^{-4}$; (3) 3.1×10^{-4}; (4) 6.2×10^{-4}; (5) 9.3×10^{-4}; (6) 1.24×10^{-3}; (7) 1.55×10^{-3}; (8) 217×10^{-3}; (9) 2.48×10^{-3}; (10) 3.1×10^{-3}; and (11) 3.72×10^{-3} M.

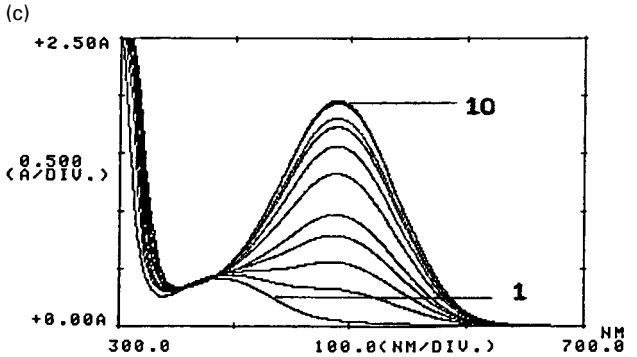
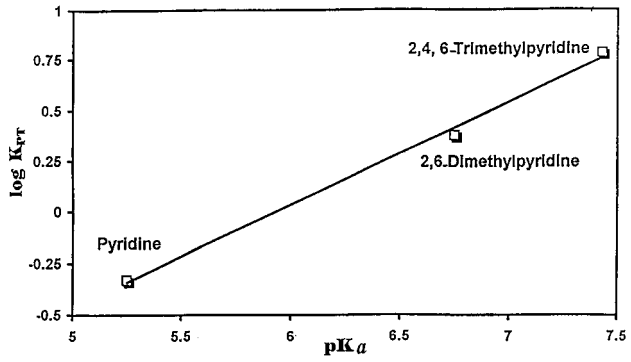


Fig. 1c Absorption spectra of 5×10^{-3} M DHBQ in 1,4 dioxan in presence of various concentrations of triethylamine: (1) 0,0; (2) 2.3×10^{-4}; (3) 4.6×10^{-4}; (4) 6.9×10^{-4}; (5) 9.2×10^{-4}; (6) 1.38×10^{-3}; (7) 1.84×10^{-3}; (8) 2.3×10^{-3}; (9) 2.7×10^{-3}; and (10) 3.2×10^{-3} M.

in the amine concentration, a new band appears at the long wavelength region corresponding to the proton transfer complex. The proton transfer band shifts bathochromically depending on the amine strength. One isosbestic point was recorded in the electronic spectra in Fig. 1, proving the formation of 1:1 proton transfer equilibrium between DHBQ and the investigated amines. It can be represented by the following equation:

$$\underset{\text{(DHBQ)}}{\text{HOBQOH}} + NR_3 \rightleftharpoons \underset{\text{(A)}}{\text{HOBQOH}.....NR_3} \rightleftharpoons \underset{\text{(B)}}{\text{HOBQ}\bar{\text{O}}...\ H^+NR_3}$$



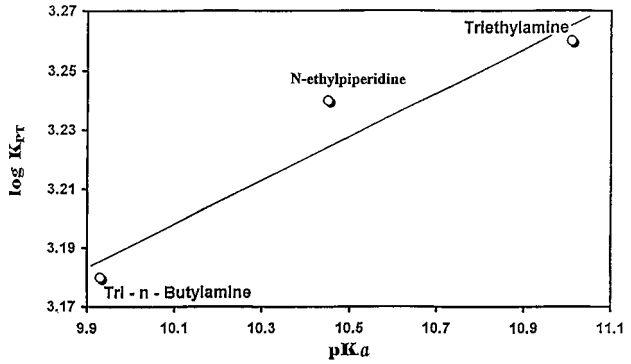


Fig. 2 Correlation between log K_{PT} and p*K*a.

The establishment of another equilibrium including the ions $HOBQ\bar{O}$, H^+NR_3 and the proton transfer species (B) probably does not occur. This assumption is based on the lower dielectric constant of 1,4-dioxane, the lower p*K* values of DHBQ together with the absence of a second isosbestic point in the electronic spectra presented in Fig. 1. Hence the studied proton transfer equilibrium constant K_{PT} can be represented by the following equation:

$$K_{PT} = \frac{[HOBQO^-...H^+NR_3]}{[HOBQOH][NR_3]}$$

In Table 1, the amines, their aqueous pK_a values, the proton transfer equilibrium constants, the proton transfer band λ_{max}, the position of the isosbestic point, together with the concentration range are collected. The relationship between the logarithm of the equilibrium constants and the basicity of the amines is presented in Fig. 2. Two lines were obtained, the lower one represents the aliphatic tertiary amine complexes having higher K_{PT} values. The upper line represents the aromatic tertiary amine complexes having lower K_{PT} values. The lower pK_a values and the *ortho*-methyl substituent effect are presumably responsible for the lower K_{PT} values for aromatic tertiary amine complexes. The effect of temperature on the proton transfer process from DHBQ to 2,6-dimethylpyridine, 2,4,6-trimethylpyridine, tri-*n*-butylamine and triethylamine in 1,4-dioxane was studied. The thermodynamic parameters were estimated and gathered in Table 2.

Table 2, shows the nice correlation between the enthalpy of proton transfer complex formation $-\Delta H^o$ and the pK_a of the amines where increasing the pK_a increases $-\Delta H^o$. The small negative values of the enthalpies for tertiary aromatic amines proton transfer complex formation 4.8 and 7.8 kJ/mol suggested a weak hydrogen bond in these complexes.

Table 1 Electronic spectral data for hydrogen-bonding interaction between DHBQ and aromatic, aliphatic tertiary amines

Amine	pK_a	K_{PT}	λ^{max}(PT)/nm	Isosbestic point/nm	Conc range/M
Pyridine	5.25	0.46	450	351	0.124–1.695
2,6-Dimethylpyridine	6.75	2.37	456	360	0.086–2.146
2,4,6-Trimethylpyridine	7.43	6.07	460	371	0.037–0.75
Tri-*n*-butylamine	9.93	1530	489	381	$1.55 \times 10^{-4} - 3.72 \times 10^{-3}$
N-Ethylpiperidine	10.45	1720	491	384	$16 \times 10^{-5} - 1.92 \times 10^{-3}$
Triethylamine	11.01	1825	493	392	$2.3 \times 10^{-4} - 3.22 \times 10^{-3}$

Table 2 Thermodynamic parameters for the hydrogen bonding interaction between DHBQ and some aromatic, aliphatic tertiary amines

Amine	Enthalpy–$\Delta H°$/kJmol	Entropy–ΔS°/J/K	Free energy–$\Delta G°$/kJ/mol
2,6-Dimethylpyridine	4.8	8.89	2.15
2,4,6-Trimethylpyridine	7.8	11.74	4.3
Tri-*n*-butylamine	23.42	17.28	18.27
Triethylamine	29.27	35.5	18.69

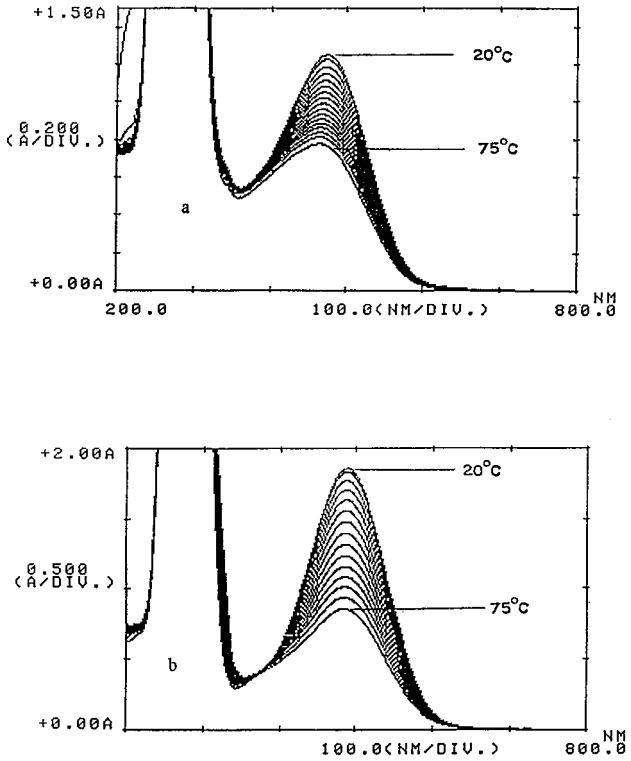


Fig. 3 Effect of temperature on the proton transfer band from 20 to 75°C for 5×10^{-3} M DHBQ and 2×10^{-3} M. (a) 2,4,6 trimethylpyridine and (b) triethylamine.

The lower negative values of the entropies in tertiary aromatic amine proton transfer complexes Table 2, reflect less hindered complexes thus confirming the presence of only one species, the proton transfer complex ($HOBQO^-\ldots HNR^{3+}$). For tertiary aliphatic amines proton transfer complex formation with DHBQ, the enthalpy of formation reached –23.42 and –29.27 kJ/mole for tri-*n*-butylamine and triethylamine complexes respectively suggesting moderately strong hydrogen bonds in such complexes. The entropies of formation for these complexes recorded moderate values –17.28 and –35.5 J/K confirming the presence of one species, the proton transfer complex ($HOBQO^-\ldots HNR^{3+}$). Although TEA is less hindered than tri-*n*-butylamine, its $-\Delta S^o$ reached a value 35.5 J/K twice time that for $-\Delta S^o$ in tri–*n*-butylamine complex 17.28 J/K. This result can be interpreted in terms of an amine solvated proton transfer complex, where DHBQ and TEA molecules are involved.[21]

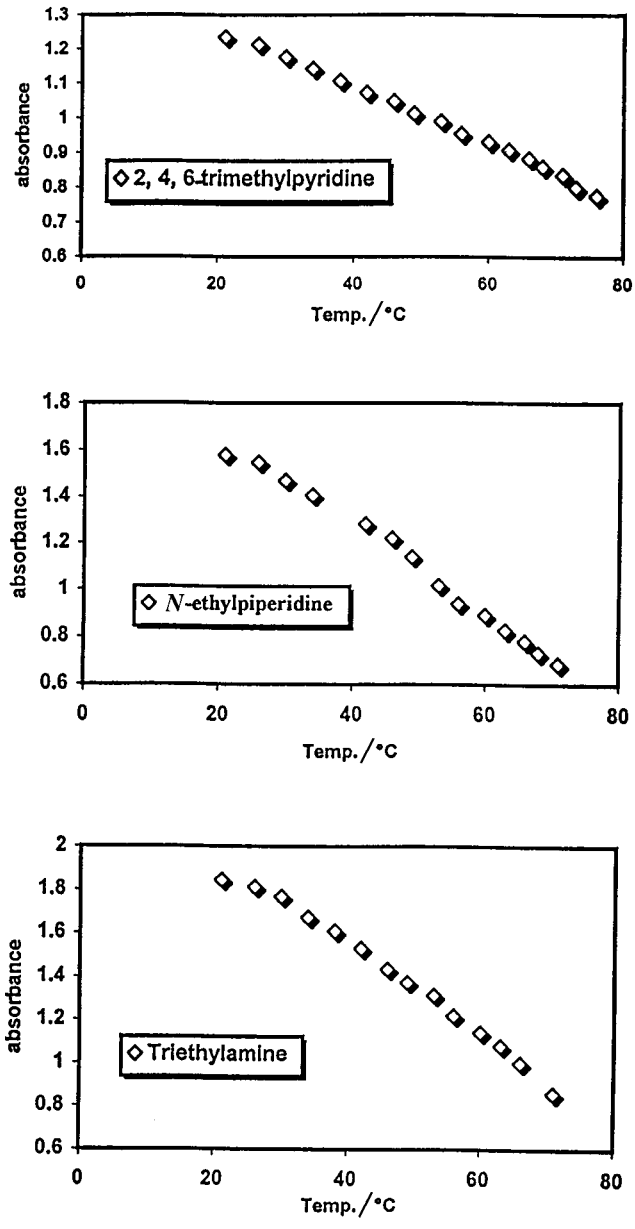


Fig. 4 Correlation between temperature and absorbance.

The effect of temperature on the proton transfer band was analysed for 2,4,6-trimethylpyridine, *N*-ethylpiperidine and triethylamine –DHBQ hydrogen bonded complexes. The

concentration of the amines was 2×10^{-3} M and the concentration of DHBQ was 5×10^{-3}M. The temperature range was 20–75°C in 1,4 –dioxane. Fig.3 represents examples of the temperature effect on the proton transfer band for DHBQ-2,4,6-trimethypyridine (Fig. 3a) and triethylamine complexes (Fig. 3b). It is clearly observed in Fig. 3, that increasing the temperature decreases the absorbance of the proton transfer band where the proton transfer equilibrium shifts towards the molecular species. The correlation between the absorbance and the temperature for the studied complexes is presented in Fig. 4 where a linear relationship is obtained. It has been found that the slope of the line representing the trimethylpyridine complex, –0.007, is higher than that representing *N*-ethylpiperidine and triethylamine complexes, –0.02. These results reflected the higher sensitivity of the proton transfer equilibrium to shift towards the molecular species OH….NR_3 in aromatic tertiary amine complexes and towards the proton transfer species O^-……H^+NR_3 in aliphatic tertiary amine complexes.

The solvating effect on the proton transfer equilibrium between DHBQ and amines was studied through the hydrogen bonding interaction between DHBQ and some aminopyridines in different mixed solvents. These mixtures included 70% benzene and 30% electron donating solvents ethylacetate, acetone, dimethylformamide and dimethyl sulfoxide respectively. In all the electronic spectra the proton transfer band appeared near 500 nm and only one isosbestic point was recorded confirming the presence of a 1:1 proton transfer equilibrium.

Although 2-aminopyridine and 2,4,6-trimethypyridine have similar pK_a values, the proton transfer equilibrium constants K_{PT} between 2-aminopyridine and DHBQ recorded very high values compared with that for 2,4,6-trimethylpyridine-DHBQ in 1,4-dioxane. The results confirm the solvent-solute hydrogen bond formation between the amino group hydrogen and the electron donating solvent (short-range salvation effect). This effect increases the electron density on the amino group nitrogen atom producing higher electron density on the ring nitrogen through resonance and inductive effects. Hence K_{PT} values increased sharply as shown in Table 3. It has been found that K_{PT} in 70% benzene and 30% ethylacetate mixture reached twice the values in the presence of 70% benzene and 30% acetone although they have similar β values.

These results can be rationalized in terms of short-range solvation between the electron donating solvents and the *N*-hydrogen of 2-aminopyridine species that are simultaneously participating in a proton transfer complex formation with DHBQ. On the other hand, solvation interaction can occur with DHBQ. It seems that in presence of ethylacetate, its two oxygen atoms retard the hydrogen bonding solvation with DHBQ and consequently the solvation interaction occurs with the *N*-hydrogen of 2-aminopyridine leading to a higher K_{PT} value 1141. In the presence of acetone, solvation occurs with both the *N*-hydrogen and DHBQ in the formed proton transfer complex hindering the proton transfer process and producing a lower K_{PT} value, 589. Although DMSO and DMF are among the strongest solvators and K_{PT} raisers, lower values of K_{PT} were recorded compared with those in the presence of acetone and ethylacetate, Table 3. One concludes that the solvation interaction occurs only between DMSO or DMF and the likely solvated DHBQ, inhibiting the proton transfer process and leading to a sharp decrease in K_{PT} values. A discrepancy was found between the present results and those published by Scott *et al.*[17,22] In these authors' work, the solvation interaction between DMF and DMSO occurs only with the secondary or primary amines hydrogen (s) while the solvation with 2,4-dinitrophenol completely disappears, producing higher K_{PT} values. To get complementary evidence of intermolecular hydrogen bond between the electron donating solvents and the reactants (DHBQ and 2-aminopyridine), the thermodynamic parameters for the proton transfer complex formation in the different mixed solvents were estimated. The data are collected in Table 3, and depicted graphically in Fig. 5.

It is shown from Table 3 that $-\Delta H^o$ recorded higher values in the presence of ethylacetate and acetone confirming the formation of strong proton transfer complexes with higher K_{PT} values. In the presence of DMSO and DMF, the enthalpy reached lower negative values confirming the formation of weak proton transfer complexes with lower K_{PT} values. As clearly observed in Table 3, the entropy of proton transfer complex formation between 2-aminopyridine and DHBQ is going in concert with the previous results; it reached lower negative values in presence of ethylacetate, DMSO and DMF asserting that the solva-

Table 3 Thermodynamic parameters for the formation of hydrogen- bonded complexes between DHBQ and 2-aminopyridine in different mixed solvents

T°C	K_{PT}	*R* ln *K*	$-\Delta H°$/kJ/mol	$-\Delta G°$/kJ/mol	$-\Delta S°$/J/K	Mixture
25	1141	14.08	40.98	17.55	78.62	30% ethylacetate 70% + benzene
30	866	13.53				
35	614	12.84				
40	475	12.33				
45	347	11.70				
25	589	12.76	50.184	15.90	114	30% acetone + 70% benzene
30	463	12				
35	304	11.44				
40	222	10.81				
45	164	10.20				
20	123	9.63	19.79	11.66	54.56	30%DMF + 70% benzene
25	107	9.36				
30	94	9.10				
35	95	8.90				
40	74	8.62				
50	41	8.15				
25	163	10.19	29.27	12.69	55.63	30% DMSO + 70% benzene
30	138	9.81				
35	113	9.47				
40	106	9.33				
45	81	8.8				
50	68	8.44				

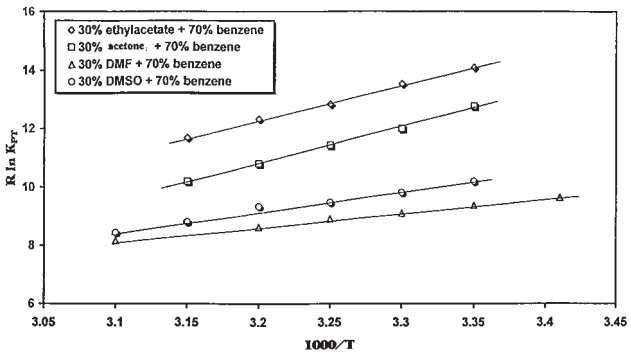


Fig. 5 Correlation between R ln K and 1000/T

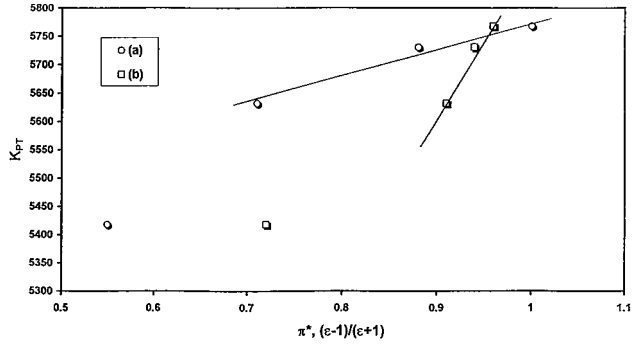


Fig. 6 Correlation between K_{PT} and Taft π* parameter (a) and Onsager parameter (ε–1)/(ε+1) (b).

tion interaction occurs with 2-aminopyridine (in presence of ethylacetate) or with DHBQ (in presence of DMSO or DMF). Hence less hindered proton transfer complexes are produced. In the presence of acetone the entropy recorded a higher negative value confirming that the interaction takes place with both the *N*-hydrogen and DHBQ. Hence a more hindered proton transfer complex is produced.

The proton transfer equilibrium between triethylamine (TEA) and DHBQ was studied in the previous mixed solvents where the proton transfer band appeared at 500 nm and one isosbestic point was recorded confirming the presence of a 1:1 proton transfer equilibrium. Without amine nitrogen protons, there is no site of hydrogen bonding with the electron donating solvent, so such an increase in K_{PT} as occurs is ascribed to the long-range solvation effect. The order of increasing in K_{PT} in 70% benzene and 30% electron donating solvents was as follows, benzene-DMSO>DMF> acetone>ethylacetate. This trend is certainly attributed to the difference in the dielectric constants and Taft's π-parameters (long-range solvation effect). The K_{PT}, Taft's π-parameters, dielectric constants ε and Onsager parameters for the different electron donating solvents are collected in Table 4. The correlation between K_{PT} and

$$\pi^*, \quad \frac{\epsilon - 1}{\epsilon + 1}$$

is presented in Fig. 6 where a linear correlation was found. A deviation was recorded in a benzene-ethylacetate mixture, which could be ascribed to the lower dielectric constant of ethylacetate compared with the other solvents.

Comparing K_{PT} values for the proton transfer complex formation between DHBQ and TEA, 2-aminopyridine in the different mixed solvents, one concludes that the inductive effect of the three alkyl groups increases K_{PT} more than the short range solvation effect between the solvents and the amino group hydrogen. The steric hindrance, the intramolecular hydrogen-bonding together with the lower pK_a of 2-aminopyridine compared with that for TEA are presumably responsible for this difference. On the other hand, the solvation interaction between the investigated Lewis base solvents and DHBQ is inhibited leading to higher K_{PT} values, Table 4. The solvation effect on the proton transfer equilibrium constant between DHBQ and 4-aminopyridine, *o*-methylaminopyridine and TEA in 30% DMSO or DMF and 70% benzene mixtures was investigated. The proton transfer band appeared near 500nm and one isosbestic point was recorded confirming the presence of a 1:1 proton transfer equilibrium. It has been found that K_{PT} recorded higher values for 4-aminopyridine and *o*-methylaminopyridine compared with that for TEA in 30% DMSO and 70% benzene mixture, Table 5. These results could be interpreted in terms of hydrogen bond formation between the amino group hydrogens and two molecules of DMSO in 4-aminopyridine-DHBQ proton transfer complex. Hence the electron density increases on the ring nitrogen through resonance and inductive effects. The K_{PT} value in the case of *o*-methylaminopyridine recorded a higher value than those for 4-aminopyridine and TEA. One remembers that the resonance between the amino group and the pyridine ring is inhibited due to the presence of the methylene group. Hence the hydrogen bonding solvation increases the electron density of the amino group nitrogen producing a higher K_{PT}. In the presence of 30% DMF and 70%benzene, the situation is completely different. It seems that DMF molecules undergo self-association via H-bonding to form dimers and higher aggregates, both cyclic and linear[23] along with the possibility of short-range solvation between the DMF hydrogen and the carbonyl of DHBQ. This behaviour of DMF is presumably responsible for the lower K_{PT} values between DHBQ and 4-aminopyridine and *o*-methylaminopyridine compared with TEA, where K_{PT} TEA> o-methylaminopyridine ≅ 4-aminopyridine, Table 5.

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Table 4 Proton transfer equilibrium constants, Taft parameters and onsager parameter for hydrogen bonding interaction between TEA and DHBQ in different solvent mixtures

70% benzene + 30% solvent	Π*	ε	$\frac{\epsilon-1}{\epsilon+1}$	K_{PT}
Ethylacetate	0.55	6.02	0.72	5418
Acetone	0.71	20.7	0.91	5632
DMF	0.88	37.2	0.94	5731
DMSO	1	45	0.96	5767

Table 5 Proton transfer equilibrium costants for DHBQ and TEA, 4-amino, *o*-methylaminopyridines proton transfer complexes in 70% benzene and 30% DMF, DMSO mixtures

Mixture	Amine	K_{PT}
70% benzene + 30% DMSO	TEA	5767
	4-aminopyridine	6133
	o-methylaminopyridine	7394
70% benzene + 30% DMF	TEA	5731
	4-aminopyridine	4156
	o-methylaminopyridine	4002

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