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Spectrophotometric determination of the transition system for interactions involving model —O—H$\cdots$N$\ll$ hydrogen bonds in acetonitrile

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ABSTRACT: The —O—H$\cdots$N$\ll$ bonds formed by interactions of picric acid (HA) with each of 12 (un)substituted pyridines (B) in acetonitrile (AN) were studied by UV–vis spectrophotometry to determine the $\Delta pK_a^{AN} = pK_{BH^+}^{AN} - pK_{HA}^{AN}$ corresponding to the transition system. The choice of both model system and experimental technique enabled the effect of heteroconjugation to be observed and the effects of formation of two theoretically possible homoconjugates (AHA^- and BHB^+) to be eliminated. The relationship between the wavelength at the absorbance maximum (λ_{max}) for 10^{-4} M solutions of complexes of picric acid with (un)substituted pyridines in acetonitrile and ΔpK_a^{AN} was found to have a sigmoidal shape with an inflection point at ΔpK_a^{AN} of ca −0.3. On the basis of this relationship and UV–vis spectra, the picric acid–3-acetylpyridine system was recognized as that being the nearest to the transition system. The fact that the transition ΔpK_a^{AN} was lower than zero has been explained by the remarkable effect of species having the average structures $A^-\cdots{}^+HB$ on the established λ_{max} values. The general results of this work and our previous results based on IR and ^{1}H NMR studies, and also the lack of any experimental counterexamples, indicate that the zero value of ΔpK_a^{AN} constitutes a fundamental basis for predicting which one, among the given family of protonic hetero systems, is the most likely to show transitional properties in acetonitrile. Finally, it is postulated that the protonic hetero systems which are the most likely to show transitional properties in a given solvent S are those for which ΔpK_a^S is close to zero, the eventual shift arising from peculiarity of the technique applied. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: UV–vis spectroscopy; —O—H$\cdots$N$\ll$ hydrogen bonds; proton exchange; transition system; solvent interactions; acetonitrile

INTRODUCTION

The symmetry of hydrogen bonds has been the subject of a wide discussion in monographs[1–5] and review articles[6,7] for over 40 years. Recent proposals to explain the possible role of strong hydrogen bonds in enzymatic catalysis[8–11] followed by a controversial debate[12–18] resulted in studies[19–23] on very subtle properties related to this problem. Indeed, according to many researchers, the most effective catalytic action has generally been expected in cases of strong hydrogen bonds in which both moieties competing for the key proton show comparable affinity to it. Although there are many possible criteria for hydrogen bond symmetry, the one that is based on the most abrupt change of physicochemical properties of the equimolar proton donor (HA)–proton acceptor (B) system with ΔpK_a (defined as $pK_{BH^+} - pK_{HA}$) is the easiest to verify and therefore seems to be the most reasonable. The first experiment illustrating such a change was carried out by Barrow[24] in his pioneering work on carboxylic acid–pyridine systems in chloroform. The measured frequency of the stretching mode was, however, referred to the solvent used, while ΔpK_a was referred to an aqueous medium. Analogous 'mixed-media relationships' were later established by a large number of investigators. It must be stressed that ΔpK_a values referred to organic solvents may appear to be strikingly different from those referred to water. For example, in water the proton-donating properties of the trimethylammonium cation (BH^+) and phenol (HA) are comparable ($pK_{BH^+}^{H_2O} = 9.8$;[25] $pK_{HA}^{H_2O} = 10.0$[26]), whereas in acetonitrile the former appears to be much stronger proton donor than the latter ($pK_{BH^+}^{AN} = 17.6$;[27] $pK_{HA}^{AN} = 26.6$[27]). In acetonitrile, the trimethylammonium cation is an even stronger proton donor than 4-nitrobenzoic acid (HR) for which pK_{HR}^{AN} is 18.7.[27] The examples given above explain why the experimental results obtained in

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non-aqueous solvents but related to $\Delta pK_a^{H_2O}$ are not comparable and hence do not allow any constructive conclusions about the localization of the hydrogen bridge to be drawn.

The two basic types of curves which illustrate the relationship between the measured value and ΔpK_a^S (where S denotes solvent used) are (a) the sigmoidal curve with an inflection point[24,28–30] and (b) the deltian curve with a maximum,[31–39] although in some studies it appeared to be of gaussian shape.[28,30,31] Each of these two curves would allow for the transition system within the given family systems to be detected. None of them is, however, reached when the logarithm of the formation constant of AHB or AHA_1^- complexes in the solvent S is plotted against ΔpK_a^S. In that case, the relationship is practically linear with only insignificant deviations caused by differentiated steric hindrances.[40–42] Apparently, the reason is that the two related values, $\log K_{AHB}^S$ and ΔpK_a^S do have the same thermodynamic origin and consequently undergo proportional changes when passing throughout whole family systems. It is then very fortunate that selected spectroscopic properties of protonic hetero systems appear to be much more sensitive than those of thermodynamic ones.

In IR studies, the most often measured values are the frequency of one chosen stretching band at the absorbance maximum[24,28,29,43,44] and position of the centre of gravity of a broad continuum.[31,32,45] The latter approach seems to be more reliable, as it allows one to avoid the problems caused by the fact that in one system the position of the absorbance maximum is settled by the band coming from the heteroconjugate, whereas in another it may be settled by the predominant band coming from one of the two possible homoconjugates. Its disadvantage is that some particular species, unlike others, may contain additional groups (e.g. nitro groups) hardly participating in the formation of hydrogen bonds but contributing to the broad continuum and thus affecting the position of its centre of gravity.

In ^{1}H NMR studies, the typically measured value for an equimolar mixture of proton donor and proton acceptor is the weighted average proton chemical shift.[28,30,33–39,46] The use of chemical shift increments[29] reflects the effect of the hydrogen bond formation itself, as it takes into account the initial state of the key proton, but simultaneously leads to a major problem in the reliable determination of the limiting values of the proton chemical shifts for particular proton donors. Undoubtedly, the great advantage of the ^{1}H NMR technique is the fact that if the concentration of water is low enough, the observed key peak appears at a sufficiently low magnetic field not to be overlapped by others (e.g. those characteristic of aromatic protons).

The results obtained by IR and ^{1}H NMR techniques for equimolar 4-nitrobenzoic acid–substituted phenolate systems in acetonitrile[30] appears to be, so far, the only significant one which relates the measured value to the ΔpK_a referred to the solvent used. The respective IR spectra showed that with increasing ΔpK_a^{AN}, a gradual frequency shift ($\Delta\nu$) occurs, along with the disappearance of the band corresponding to stretching mode in the carboxyl group. Simultaneously, bands corresponding to stretching modes (symmetrical and asymmetric) in the carboxylate group appeared. As a result, in the corresponding graphs of $\Delta\nu$ as a function of ΔpK_a^{AN} some kind of discontinuity was found. The distribution of points was indicative of two sigmoidal curves starting from the same point but ending up at different ‘saturation values’ which represented symmetrical and asymmetric stretching modes of the carboxylate group. In the ^{1}H NMR spectra of the same systems a very characteristic curve with a maximum value of the averaged proton chemical shift was observed. It is essential that in both IR and ^{1}H NMR spectra the specific behaviour occurred at a ΔpK_a^{AN} which was practically equal to zero. Since we are dealing here with the transitional change in spectral properties, the specific hypothetical system in which such a change occurs will be referred to as a *transition system* and the characteristic value of ΔpK_a^{AN} will be referred to as ΔpK_a^{AN} *of transition*.

Although frequently used in studying protonic hetero systems, UV–vis spectroscopy has rarely been applied in determining transition systems.[47–50] In all relevant studies the magnitude measured was related to $\Delta pK_a^{H_2O}$. This made it difficult to draw any constructive conclusion from the results obtained. Therefore, the primary aim of this work was to check whether the previously found general result (transition system when $\Delta pK_a^{AN} = 0$) may also be confirmed for molecular protonic hetero systems by UV–vis spectroscopy. A supplementary aim was to identify the most important factors affecting the determined ΔpK_a^{AN} of transition.

The general problem with the use of UV–vis spectroscopy for determining a transition system is the same as that for the IR technique, viz. superimposition of bands coming from species other than the heteroconjugate. It can be avoided, however, if the proton donor and the proton acceptor in the system studied are chosen in such a way that the two possible homoconjugates can hardly be ‘seen’ by this technique. Such a situation exists in a selected picric acid (HA)–substituted pyridine (B) systems in acetonitrile. The homoconjugates BHB^+ and AHA^- are scarcely visible in the spectroscopic range of interest (330–450 nm), the former because it does not possess any chromophore group (colourless) and the latter because of negligible homoconjugation, as proved experimentally[51] and explained in terms of strong steric effects caused by the nitro substituents and charge delocalization.[52]

The pK_{HA}^{AN} of picric acid (11.0)[51] fits well the $pK_{BH^+}^{AN}$ range of the commonly available substituted pyridines,[27] thus enabling systems of ΔpK_a^{AN} close to zero to be studied. It is also very fortunate that the ΔpK_a^{AN} value characterizing a given HA + B system can be calculated directly from the equation

$$\Delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}} = \mathrm{p}K_{\mathrm{BH^+}}^{\mathrm{AN}} - \mathrm{p}K_{\mathrm{HA}}^{\mathrm{AN}} = \frac{E_{\mathrm{AHA^-}} - E_{\mathrm{BHB^+}}}{s} + 2\log y_{\pm} \qquad (1)$$

where $E_{\mathrm{AHA^-}}$ is the emf of the cell containing equimolar amounts of HA and $\mathrm{A^-}$, $E_{\mathrm{BHB^+}}$ is the e.m.f. of the cell containing an equimolar amounts of $\mathrm{BH^+}$ and B, s is the slope of the glass electrode calibration curve and $y_{\pm}$ is the medium ion activity coefficient. Consequently, the absolute $\mathrm{p}K_{\mathrm{HA}}^{\mathrm{AN}}$ and $\mathrm{p}K_{\mathrm{BH^+}}^{\mathrm{AN}}$ values are not even required.

EXPERIMENTAL

Acetonitrile (Serva, pure) used for the potentiometric measurements was purified as described previously.[53] Acetonitrile of spectroscopic grade (Riedel-de Haën) was used in the UV–vis studies without further purification. Picric acid (POCh, Gliwice, Poland; p.p.a.) was carefully dried over P_4O_{10} and crystallized from tetrachloromethane. Liquid pyridines (POCh; p.p.a.) were treated with KOH and distilled. The solid substituted pyridines 2-cyanopyridine (Loba Chemie, pure), 3-cyanopyridine (Windsor, pure), 4-cyanopyridine (Fluka, pure), 3-hydroxypyridine (Fluka, pure) and 4-hydroxypyridine (Fluka, pure) were crystallized from 96% ethanol (POCh, p.p.a.). Picric acid–pyridine complexes were prepared by mixing equimolar amounts of picric acid and the corresponding pyridines in ethyl acetate at 55 °C, filtration from the reaction mixture and final crystallization from ethanol. Pyridinium perchlorates were prepared carefully by mixing equimolar amounts of the corresponding substituted pyridine in methanol and perchloric acid (Ferak, Berlin, 60% aqueous), evaporation of solvents under reduced pressure and crystallization from methanol. The composition of each of the prepared picrate complex and perchlorate salt was confirmed by elemental analysis carried out with a Model 1106 elemental analyser (Carlo Erba) and melting-point corresponding to that in the literature.

E.m.f. measurements involving equimolar mixtures of substituted pyridines and their perchlorate salts and equimolar mixtures of picric acid and tetrabutylammonium picrate in the used solvent were carried out (twice for each system) at 298 K using the same equipment as described previously.[53]

UV–vis spectra were recorded on a Perkin-Elmer Model 402 spectrophotometer in quartz cells of thickness 1 cm.

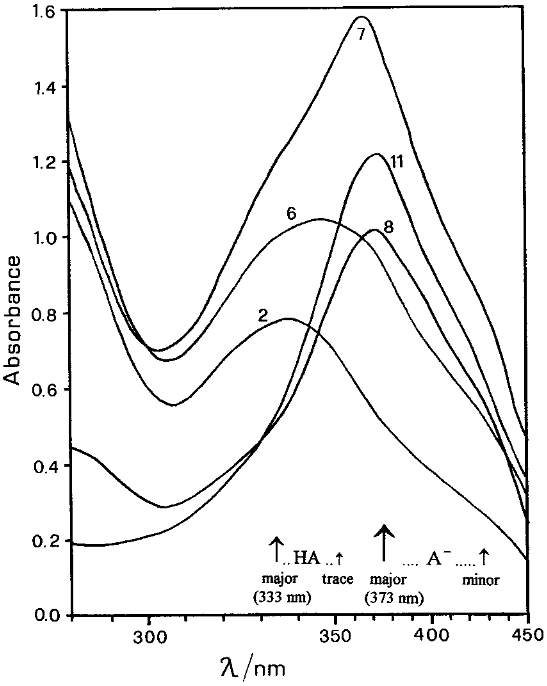

Figure 1. UV–vis spectra of acetonitrile solutions of selected complexes of picric acid with (un)substituted pyridines: (2) picric acid–2-bromopyridine ($\Delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}} = -3.31$), (6) picric acid–3-bromopyridine ($\Delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}} = -0.60$), (7) picric acid–3-acetylpyridine ($\Delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}} = -0.03$), (8) picric acid–3-hydroxypyridine ($\Delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}} = 1.59$), (11) picric acid–2-ethylpyridine ($\Delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}} = 2.55$). Analytical concentrations are 10^{-4} M

RESULTS AND DISCUSSION

Figure 1 presents the UV–vis spectra of five selected picric acid–substituted pyridine systems. With increasing $\Delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$ the position of the absorbance maximum shifts towards higher wavelengths. Since the $\lambda_{\max}$ values for solutions of picric acid (HA) and tetrabutylammonium picrate ($\mathrm{A^-}$) are 333 and 373 nm, respectively,[54] the appearance of bands between these two limiting values must result from the co-existence of other (than HA and $\mathrm{A^-}$) species in equilibrium. The effect of the $\mathrm{AHA^-}$ ions on the spectra can be excluded bearing in mind the above-mentioned evidence and explanation. The negligible homoconjugation in the picric acid–picrate systems has been widely utilized in practice for calibration of glass electrodes in non-aqueous media.[27,51] Also, the effect of the formation of $\mathrm{BHB^+}$ homoconjugates on the UV–vis spectra can safely be excluded because none of the studied species containing a B moiety (B, $\mathrm{BH^+}$ or $\mathrm{BHB^+}$) possess any chromophoric group permitting significant absorption in the spectroscopic range of interest. The only species which could possibly affect the observed spectra are those which contain both picric acid and pyridine moieties bonded together, presumably through hydrogen bonding, although the formation of charge-transfer complexes seems worth considering.

According to the commonly accepted point of view,[5] the hydrogen bonding equilibria are expressed in terms of the scheme:

$$\begin{aligned}\mathrm{HA + B} &\rightleftharpoons \mathrm{AH\cdots B} \rightleftharpoons \mathrm{A^- \cdots {}^+HB}\\ &\rightleftharpoons \mathrm{A^- + BH^+}\end{aligned} \qquad (2)$$

of which the central one, between two tautomeric forms $\mathrm{AH{\cdots}B}$ and $\mathrm{A^-{\cdots}{}^+HB}$, has been called the proton transfer equilibrium. The most commonly cited evidence for this equilibrium, given by Baba *et al.*,[55] has, however, been easily questioned[56] as conflicting with the chemical equilibrium law; the relative intensity of the two bands assigned to the $\mathrm{AH{\cdots}B}$ and $\mathrm{A^-{\cdots}{}^+HB}$ forms appeared to be strongly dependent on the analytical concentrations of HA and B. So far, no really convincing evidence for the existence of this equilibrium has been published. The proton transfer equilibrium is, anyway, difficult to use in explaining the solution spectra of selected pyridine picrates shown in Fig. 1. If it were really so significant, both the short-wave band (corresponding to $\mathrm{AH{\cdots}B}$) and long-wave band (corresponding to $\mathrm{A^-{\cdots}{}^+HB}$) should be very characteristic at least for systems 6, 7 and 8 showing the most transitional properties. Meanwhile, in the spectrum for system 6 the band corresponding to the form $\mathrm{A^-{\cdots}{}^+HB}$ is hardly visible and in the spectrum for system 8 the band corresponding to the form $\mathrm{AH{\cdots}B}$ is hardly visible. If one assumes that in the spectrum for system 6 the hump at ca 410 nm is caused mainly by $\mathrm{A^-{\cdots}{}^+HB}$ and that in the spectrum for the system 8 the hump at ca 330 nm is caused mainly by $\mathrm{AH{\cdots}B}$, then the same assignment should be made for the spectrum of system 7. In that case, however, there is the question of what kind of species is represented by the band with $\lambda_{\max}$ at ca 366 nm. It is very doubtful that we are dealing here with the triple minimum proton potential. The eventual effect of coalescence of the two bands (corresponding to $\mathrm{AH{\cdots}B}$ and $\mathrm{A^-{\cdots}{}^+HB}$ forms) in the spectrum for system 7, to form one central band, seems unlikely, first, because of the sharpness of this band (despite the strong influence of both side humps), second, because of a complete lack of any indication of this effect in the cases involving systems 6 and 8, and third, under such an assumption, there are two significant side humps which must be explained in terms of species other than $\mathrm{AH{\cdots}B}$ and $\mathrm{A^-{\cdots}{}^+HB}$. Even considering that this coalescence occurs in the spectrum of system 7, what use can one make of the proton transfer equilibrium approach? The coalescence of bands originating from both tautomeric forms of the H-bonded complex has not, anyway, been characteristic of the spectra given by several other workers. For example, in the spectra given by Barrow,[24] quite the contrary, the frequencies assigned to the corresponding stretching modes in the forms $\mathrm{AH{\cdots}B}$ and $\mathrm{A^-{\cdots}{}^+HB}$ remain nearly constant throughout the whole wide $\Delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{H_2O}}$ range studied, only the optical intensities being altered.

The most reasonable explanation of the observed spectra may therefore be given assuming that although a large number of AHB forms co-exist (while the key proton is exchanged or oscillates along the AHB bridges), only one of them is dominant, thus giving rise to the appearance of only one significant band. This band is overlapped by those corresponding to other species which occur in relatively large concentrations and show sufficiently large absorptivities. Thus, in the spectra for systems 1–6 ($\Delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$ markedly negative) the band corresponding to the species with the averaged structure $\mathrm{AH{\cdots}B}$ overlaps the bands corresponding to HA and AHS, the others (those of $\mathrm{A^-}$ and $\mathrm{SA^-}$) being negligible. In the spectra of systems 8–12 ($\Delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$ markedly positive) the band corresponding to the species with the averaged structure $\mathrm{A^-{\cdots}{}^+HB}$ overlaps the bands corresponding to $\mathrm{A^-}$ and $\mathrm{SA^-}$, the others (those of HA and AHS) being negligible.

The only spectrum with the absorbance maximum lying in an intermediate spectral range is that for the picric acid–3-acetylpyridine system, for which $\Delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$ is very close to zero. Therefore, of all complexes studied only this particular one may be given the extended formula $\mathrm{A{\cdot}H{\cdot}B}$, which indicates the presence of the hydrogen bridge being close to symmetrical. This system may therefore be regarded as very close to the transition system for the picric acid–pyridine interactions. The complexes studied for which $\Delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$ is sufficiently negative may consequently be represented by the extended formula $\mathrm{AH{\cdots}B}$ and those for which $\Delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$ is sufficiently positive by the extended formula $\mathrm{A^-{\cdots}{}^+HB}$.

The results of e.m.f. measurements used for determining $\Delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$ according to Eqn. (1) and wavelengths at the absorbance maximum for 10^{-4} M solutions of picric acid–(un)substituted pyridines in acetonitrile are given in Table 1. Bearing in mind the low analytical concentration range studied, and that in systems with $\Delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$ close to zero a significant part of the co-existing species remain in the non-ionized form, the medium activity coefficient in Eqn. (1) was assumed to be equal to unity. The $\Delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$ values were used for rough calculations of heteroconjugation constants $K_{\mathrm{AHB}} = [\mathrm{AHB}]/([\mathrm{HA}][\mathrm{B}])$ of the corresponding picric acid–(un)substituted pyridine complexes. Since the complete solution to the heteroconjugation problem is currently not available (no experimental method successfully takes into account the formation of solvates), the most reasonable way to make such a calculations is to use the relationship

$$\frac{K_{\mathrm{AHB}}^{2}}{K_{\mathrm{AHA^-}} \cdot K_{\mathrm{BHB^+}}} = \alpha \frac{K_{\mathrm{HA}}}{K_{\mathrm{BH^+}}} \qquad (3)$$

This type of relationship was originally deduced previously[56] and receives strong confirmation from the experimental results. The dependences between the heteroconjugation constant for a family of systems and

Table 1. Wavelengths at the absorbance maximum (λ_{max}) for solutions of picric acid–(un)substituted pyridine complexes in acetonitrile ($C_{AHB} = 10^{-4}$ M), results of e.m.f. measurements used for determining ΔpK_a^{AN} and corresponding heteroconjugation constants $K_{AHB} = [AHB]/[HA][B]$

No.	(Un)substituted pyridine moiety	λ_{max} (nm) (±2 nm)	E_{BHB^+} (mV)[a]	ΔpK_a^{AN}[b]	Log K_{AHB}[c]
1	2-Cyanopyridine	334	757.3	−3.95	1.0
2	2-Bromopyridine	337	719	−3.31	1.3
3	3-Cyanopyridine	338	686.8	−2.77	1.6
4	4-Cyanopyridine	337	656.5	−2.26	1.9
5	2-Acetylpyridine	345	584.3	−1.05	2.5
6	3-Bromopyridine	347	557.3	−0.60	2.7
7	3-Acetylpyridine	366	523.3	−0.03	3.0
8	3-Hydroxypyridine	372	426.5	1.59	3.8
9	Pyridine	372	420.5	1.69	3.81[d]
10	4-Hydroxypyridine	373	418.8	1.76	3.9
11	2-Ethylpyridine	373	369.3	2.55	4.3
12	4-Ethylpyridine	373	341	3.03	4.5

[a] The e.m.f. of the cell containing an equimolar mixture of (un)substituted pyridine (B) and $BH^+ClO_4^-$ ($C_B = C_{BH^+ClO_4^-} = 1.00 \times 10^{-3}$) (the average of two measurements).

[b] $\Delta pK_a^{AN} = pK_{BH^+}^{AN} - pK_{HA}^{AN}$ calculated directly from Eqn. (1), where E_{AHA^-} (e.m.f. of the cell containing equimolar mixture of HA and $Bu_4N^+A^-$, $C_{HA} = C_{Bu_4N^+A^-} = 1.00 \times 10^{-3}$) was equal to 521.5 mV and s (the slope of the glass electrode calibration curve) was equal to 59.68 mV pH^{-1}.

[c] Calculated from the relationship $K_{AHB}^2/K_{AHA^-} \cdot K_{BHB^+} = \alpha(K_{HA}/K_{BH^+})$ (see text).

[d] Ref. 55.

ΔpK_a (related to the solvent used) are linear, with a slope typically close to 0.5.[40–42,57] For molecular protonic hetero systems, unlike ionic systems, the coefficient α, however, differs significantly from unity.[42] To find its current value (once better methods for determining heteroconjugation constants have been developed, the value of this coefficient should accordingly be adjusted), one can therefore use the constants determined previously by Chantooni and Kolthoff [$K_{AHB} = 6.4 \times 10^3$ (Ref. 54), $K_{AHA^-} = 2$ (Ref. 51), $K_{BHB^+} = 7$ (Ref. 54)] and the ΔpK_a^{AN} values determined in this work for the picric acid–(un)substituted pyridine system in acetonitrile. Transforming Eqn. (3) to the form

$$\log\alpha = 2\log K_{AHB} - \log K_{AHA^-} - \log K_{BHB^+} - \log\left(\frac{K_{HA}}{K_{BH^+}}\right) \qquad (4)$$

and substituting $\log(K_{HA}/K_{BH^+}) = \Delta pK_a^{AN} = 1.69$, one obtains $\log\alpha = 4.8$. Homoconjugation constants for substituted pyridines fall into a very narrow range,[54,58] being at the limits of potentiometric determinations. Therefore, assuming for our rough calculations that they are the same as for pyridine, one makes an insignificant error. Under such assumptions, the final rough values of K_{AHB} are then simply related to ΔpK_a^{AN} by

$$\log K_{AHB} = 3.0 + \frac{1}{2}\Delta pK_a^{AN} \qquad (5)$$

For the equimolar picric acid–3-acetylpyridine system, ΔpK_a^{AN} is very close to zero, then $\log K_{AHB} = 3.0$. At an analytical concentration of the complex of 10^{-4} M, assuming the formation of both homoconjugates and solvates to be negligible, one obtains $[HA] = [A^-] = [B] = [BH^+] = 4.9 \times 10^{-5}$ and $[AHB] = 2.4 \times 10^{-6}$. Considering that the formation of solvates (AHS, SA^-, SHB^+ and BS) lowers the equilibrium concentrations of the two fundamental proton donors and two fundamental proton acceptors, one can easily conclude that it must also, accordingly, lower the equilibrium concentration of the key heteroconjugate below that value. In other equimolar systems, characterized by markedly negative or markedly positive ΔpK_a^{AN}, the conditions for the formation of the heteroconjugate are much worse, resulting in correspondingly lower equilibrium concentrations of the key heteroconjugate being established. This seems to reveal the whole problem in detecting significant bands for these

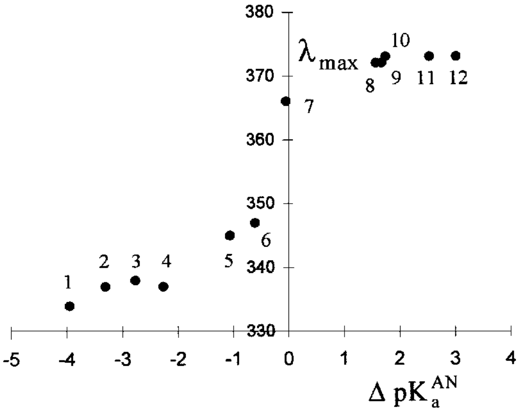

Figure 2. Relationship between λ_{max} and $\Delta pK_a^{AN} = pK_{BH^+}^{AN} - pK_{HA}^{AN}$ for selected acetonitrile solutions of picric acid (HA)–(un)substituted pyridine (B) complexes. The numbering refers to that given in Table 1

species when $\Delta\mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$ is markedly negative or markedly positive.

Figure 2 presents the relationship between wavelength at the absorbance maximum and $\Delta\mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$ for equimolar picric acid–(un)substituted pyridine systems (realized by dissolution of the corresponding pyridinium picrates) in acetonitrile. The relationship seems to have an evident sigmoidal shape. An abrupt change of $\lambda_{\max}$ appears, however, at $\Delta\mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$ close to -0.3 and not at exactly zero.

This slight shift from the previously[38] observed zero value requires a constructive explanation. Since the logarithm of the concentration ratio $[\mathrm{A}^-]/[\mathrm{HA}]$ varies linearly with $\Delta\mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$, the most probable reason for this shift is the much higher absorptivity of $\mathrm{A}^-\cdots{}^+\mathrm{HB}$ species compared with those of $\mathrm{AH}\cdots\mathrm{B}$. This, in turn, can be concluded from the fact that the picrate ion shows much higher absorptivity (1.36×10^4) than that of the picric acid molecule HA (5.95).[59] The positions of the $\lambda_{\max}$ values in the spectra shown in Fig. 1 appear as a result of the superimposition of bands coming from species of which the relative equilibrium concentrations vary when $\Delta\mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$ increases. When $\Delta\mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$ increases from negative to positive values, the structure of the key heteroconjugate changes from $\mathrm{AH}\cdots\mathrm{B}$ to $\mathrm{A}^-\cdots{}^+\mathrm{HB}$, the contribution of the latter to establishing $\lambda_{\max}$ becoming more pronounced. In Fig. 2, the relevant $\lambda_{\max}$ values for systems 7–12 are then more strongly elevated along the λ axis, with the result that the inflection point is not found at $\Delta\mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$ equal to zero but at a slightly negative value. The very characteristic asymmetric (relative to the inflection point) shape of the hypothetical curve that could be derived from the experimental points in Fig. 2 seem to confirm the reasoning given above. Regardless of this, electrostatic interactions, which do change along with $\Delta\mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$, may also contribute to the observed a symmetric distribution of the experimental points.

This work indicates that the $\Delta\mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$ value is the most important parameter affecting the physico-chemical properties of protonic hetero systems in acetonitrile. This is in full agreement with previous results based on IR and ^{1}H NMR studies. Both the maximum proton chemical shift on the graph based on ^{1}H NMR spectra and the inflection point for the corresponding curve based on IR spectra appeared at $\Delta\mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$ almost equal to zero. The same result may also be obtained when considering the analogous dependences against $\Delta\mathrm{p}K_{\mathrm{a}}^{\mathrm{H_2O}}$ found in our previous work[29] and the $\Delta\mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$ vs $\Delta\mathrm{p}K_{\mathrm{a}}^{\mathrm{H_2O}}$ relationship for benzoic acids based on data published by Kolthoff and Chantooni.[60] The rule confirmed in this work ($\Delta\mathrm{p}K_{\mathrm{a}}^{\mathrm{AN}}$ close to zero for transition $\mathrm{HA}+\mathrm{B}$ systems in acetonitrile) may also be fulfilled in a more general form: for any transition $\mathrm{HA}+\mathrm{B}$ system in the solvent S, $\Delta\mathrm{p}K_{\mathrm{a}}^{\mathrm{S}}$ is close to zero, the shift from this fundamental value arising from peculiarity of the technique applied. Confirmation of this general hypothesis by experiment for wider concentration ratios could be of great importance as it could create a basis for deriving several interesting relationships in the field of hydrogen bonding equilibria.

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