

Review Article

Proton Transfer Equilibria and Critical Behavior of H-Bonding

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Received 23 February 2012; Revised 25 April 2012; Accepted 26 April 2012

Academic Editor: Marek J. Wojcik

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The aim of the present paper is an analysis of the hydrogen bond properties for the acid-base systems depending on the ability to the proton transfer in the formulation of the Brönsted approach. After definition of the proton transfer equilibrium expressed by using the equation $\log K_{\text{PT}} = \xi \Delta pK_N$, various examples of different physical properties, such as dipole moments, IR spectra, and nuclear magnetic resonances, are presented which correlate with the ΔpK_N value. In such a way, a critical state of hydrogen bonding can be defined that corresponds to the potential of the proton motion for either single minimum or double minimum with low barrier. A particular attention in this paper found electronic spectra which have not been analysed so far and the quantitative analysis of the vibrational polarizability which can reach very high values of the order of electronic polarizability.

1. Introduction

The subject of our interest in the present review is hydrogen bonds which can be expressed as $\text{A-H} \cdots \text{B}$. It is an acid-base system in the Brönsted formulation when the A-H group is treated as an acid while the B atom or group of atoms as proton acceptor (base). The potential energy curves for the proton motion can reach various shapes, as shown in Figure 1.

The extreme curves (1) and (6) correspond to states either without proton transfer (1) or to the complete ionization when the proton is attached to B while atom A is negatively charged (6). Among the intermediate states take place those when the proton is located in the central position either with two minima (3) and a low barrier or with one single minimum (4).

There is a rich literature [1–16] with various approaches to the hydrogen bonding corresponding to different definitions, showing an increase of systems analyzed with comprehensive theoretical treatments, and containing different rich chemical characteristic features of hydrogen bonds. Most actual comprehensive review was recently published by G. Gilli and P. Gilli [16].

From the point of view of the approach based on the acid-base interaction, the substantial, parameter is the proton transfer degree which evokes changes of further

physico-chemical parameters. The main quantity is the ΔpK_a value which can be expressed in the form:

$$\Delta pK_a = pK_{\text{B}^+\text{H}} - pK_{\text{AH}} \quad (1)$$

This quantity was introduced by Huyskens and Zeegers-Huyskens [17]. We introduced normalized parameter defined as

$$\Delta pK_N = \Delta pK_a - \Delta pK_a(\text{crit}), \quad (2)$$

where $\Delta pK_a(\text{crit})$ is related to ΔpK_a region when the proton transfer degree reaches 50% [18].

The dependence of proton transfer degree on the ΔpK_N value needs a correction connected with “softness/hardness” of interaction by using parameter $\xi < 1$ [19]. The value of this parameter is the higher, the harder is the interaction reaching maximal value equal to unity. As will be seen, this quantity is well correlated with the polarizability in the transition state of hydrogen bonds. The general equation presenting the dependence of proton transfer degree on ΔpK_N possesses the form:

$$\log K_{\text{PT}} = \xi \Delta pK_N. \quad (3)$$

One should remember that physicochemical parameters measured depending on ΔpK_N and connected with the

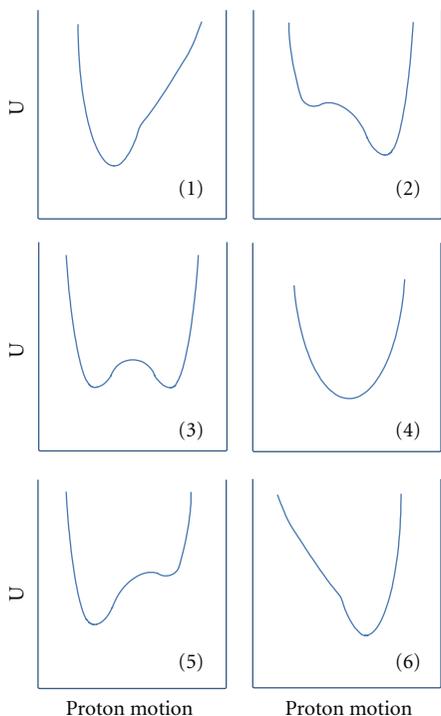


FIGURE 1: Postulated potential energy curves for the proton motion starting from nonproton-transfer state (1) up to fully ionized state (6).

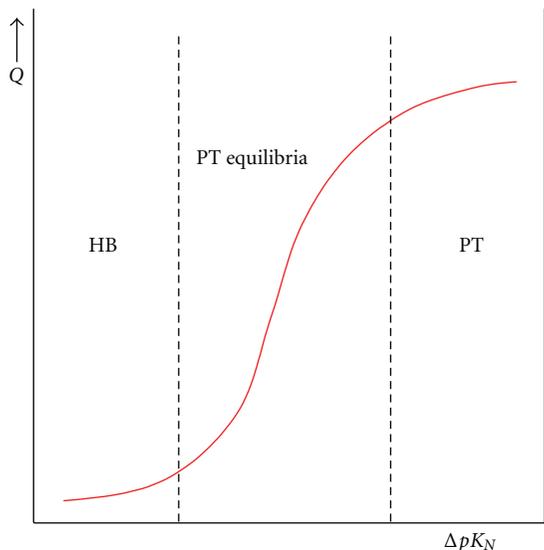


FIGURE 2: Three regions of physical properties depending on ΔpK_N : HB-related to nonproton-transfer states, PT-related to proton transfer state and HB + PT proton transfer equilibrium.

softness of interaction are related not only to ΔpK_N as has been shown in Figure 2.

There exist three regions; the central one with the equilibria of the proton transfer and side regions without proton transfer (HB) and with full ionization (PT).

Finally, as will be shown, it is necessary to mention the role of medium such as electric permittivity of the solvent

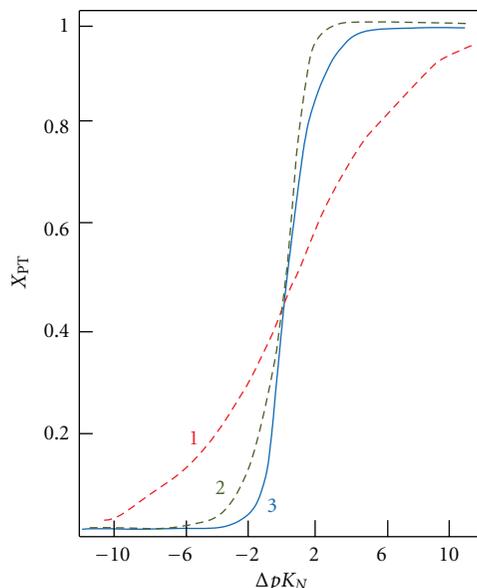


FIGURE 3: Proton transfer degree from NQR measurements for complexes composed of chlorine containing proton donors plotted versus ΔpK_N : (1) CCl_3COOH complexes ($\xi = 0.12$), (2) CHCl_2COOH complexes ($\xi = 0.42$), and (3) $\text{C}_6\text{Cl}_5\text{OH}$ complexes ($\xi = 0.74$) [20].

and specific interaction between the solute and solvent molecules.

For characterization of the role of the ξ parameter we present in Figure 3 dependencies of the proton transfer degree deduced from the measurements of nuclear quadrupole resonance (NQR) for complexes of CCl_3COOH (1) ($\xi = 0.12$), CHCl_2COOH (2) ($\xi = 0.42$), and $\text{C}_6\text{Cl}_5\text{OH}$ (3) ($\xi = 0.74$) [20]. It is well seen the property of the curves in the critical region when approaching to $\Delta pK_N = 0$.

It is justified to mention in the introduction that curves expressing dependencies of physicochemical parameters on ΔpK_N possess various shapes [18]. One can distinguish two types of correlations between the physical quantity and ΔpK_N , namely, of the sigma and delta type. The examples of such correlations will be presented in the next chapter.

2. Examples of Correlation between Physicochemical Parameters and the ΔpK_N Quantity

So far a most precisely investigated phenomenon is the dependence of the increase of dipole moment $\Delta\mu$ for complexes of phenols with N-bases. In Figure 4, we present correlation between $\Delta\mu$ and ΔpK_N obtained for a number of systems in nonpolar solvents, particularly in benzene [18]. The experimental points are adjusted to the equation [21]:

$$\Delta\mu = \frac{\Delta\mu_{\text{HB}} + b_{\text{HB}}\Delta pK_N}{1 + \exp(2.303\xi\Delta pK_N)} + \frac{(\Delta\mu_{\text{PT}} + b_{\text{PT}}\Delta pK_N) \cdot \exp(2.303\xi\Delta pK_N)}{1 + \exp(2.303\xi\Delta pK_N)}, \quad (4)$$

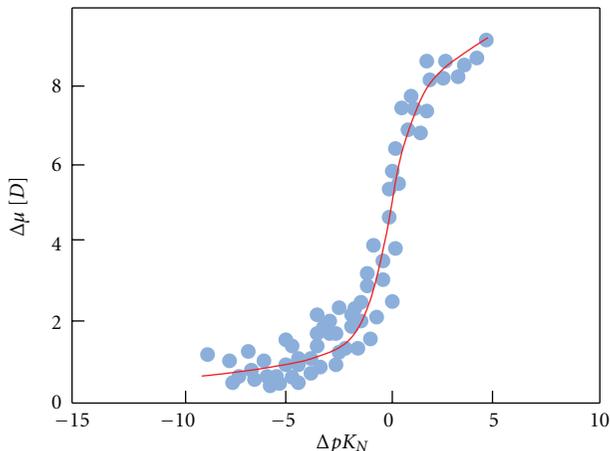


FIGURE 4: The increase of dipole moment $\Delta\mu$ plotted versus normalized parameter ΔpK_N [18].

where $\Delta\mu_{\text{HB}}$ and $\Delta\mu_{\text{PT}}$ mean the increase of the dipole moment without proton transfer (HB) and after the proton transfer (PT). These quantities depend nearly linearly on ΔpK_N with coefficients b_{HB} and b_{PT} . When approaching the critical region around $\Delta pK_N = 0$, a stepwise change of the dipole moment connected with the increase of the proton degree takes place. The proton transfer degree x_{PT} defines the equilibrium:

$$X_{\text{PT}} = \frac{\exp(2.303\xi\Delta pK_N)}{1 + \exp(2.303\xi\Delta pK_N)}. \quad (5)$$

To obtain the agreement with the experiment, it is necessary to introduce the coefficient ξ which, as has been formulated, characterizes softness/hardness of interactions. It can be, on the other hand, connected with the barrier height for the proton transfer. The value of the ξ coefficient for the case of the situation in Figure 4 equals 0.65.

Very similar run of the dependence on ΔpK_N shows the value of the ^{15}N resonance chemical shift with the ξ value equal to 0.56 [22]. However, one should remember that the results are related to markedly different experimental conditions. Thus, the results obtained for ^{15}N chemical shift were obtained for complexes of carboxylic acids with pyridine in liquefied freons.

Sigmoidal type of the relationship of physical quantity on ΔpK_N is also observed for complexes of pentachlorophenol with amines by using the nuclear quadrupole resonance (NQR) [23] that is presented in Figure 5. In addition to experimental points, there are indicated values corresponding to neat pentachlorophenol, H-bis-phenolate, as well as to Na^+ and tributylamine salts. One should remember that NQR measurements are performed for solid state that reflects observed behavior.

The similar shape of the plot with that in Figure 5 is observed between geometrical parameters of complexes and ΔpK_N and particularly between C–O bond length and ΔpK_N [25].

An example of correlation between the measured quantity and ΔpK_N of the delta type relates first of all to the proton magnetic resonance $\delta^1\text{H}$. It is presented for the

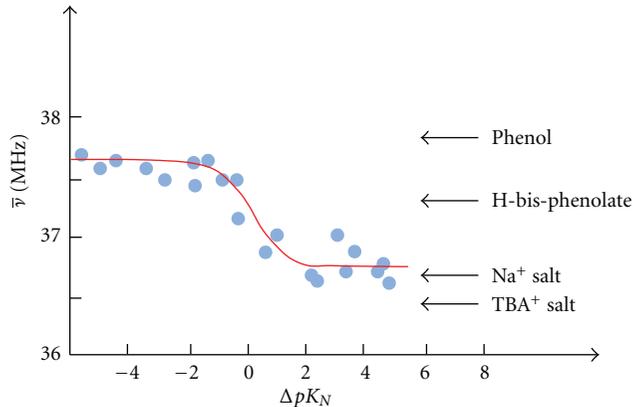


FIGURE 5: The dependence of average NQR ^{35}Cl frequency upon ΔpK_N for complexes of pentachlorophenol [24].

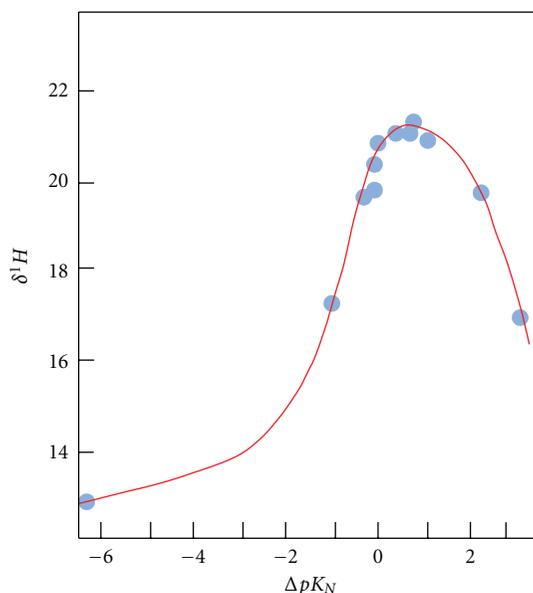


FIGURE 6: The dependence of $\delta^1\text{H}$ for complexes of carboxylic acids with pyridine in liquid freon [22].

systems analogues to the $\delta^{15}\text{N}$ resonance [18]. The experimental points of $\delta^1\text{H}$ presented in Figure 6 were obtained in the same conditions as for $\delta^{15}\text{N}$. The value of the ξ parameter is, however, somewhat lower (0.46) that we are not able to explain. From already done numerous experiments it follows that methods applied do not possess marked influence on the ξ value.

In the analysis of the correlation plots exhibiting an extremum in the critical region as in the case of $\delta^1\text{H}$, a modified approach can be used. Thus, for the description of the dependence of given physical property Q showing an extremum, the following simple procedure can be employed. The reference value of a given physical property Q is its extremum; that is, maximum or minimum. In the case of $\delta^1\text{H}$ for the systems composed of carboxylic acids and pyridine in liquid freons the maximum value equals 21.5 ppm. The delta type correlation can be transformed to the sigmoidal one by assuming that $Q(\text{crit}) = 0$, while $\Delta Q_{\text{HB}} < 0$ and $\Delta Q_{\text{PT}} > 0$ as has been done in Figure 7.

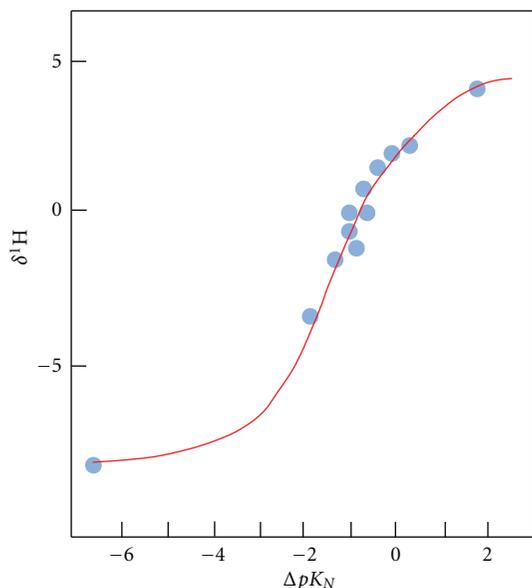


FIGURE 7: Correlation between $\delta^1\text{H}$ and ΔpK_N for complexes of carboxylic acids with pyridine in liquid freon according to (6).

The correlation between ΔQ and ΔpK_N is presented in the following equation [18]:

$$\Delta Q = \frac{\Delta Q_{\text{HB}} + \Delta Q_{\text{PT}} \exp(2.303\xi \Delta pK_N)}{1 + \exp(2.303\xi \Delta pK_N)}. \quad (6)$$

The parameters for best fitting are $Q_{\text{max}} = 21.5$ ppm $\Delta Q_{\text{HB}} = -8.3$ ppm while $\Delta Q_{\text{PT}} = 4.4$ ppm and $\xi = 0.46$ as has been already mentioned.

The properties of infra-red spectra are commonly accepted for the hydrogen bonded systems. This relates first of all to the absorption band ascribed to the stretching vibrations of either AH group (HB state) or BH^+ group (PT state). The evolution of broad absorption ascribed to the $\nu(\text{AH})$ or $\nu(\text{NH}^+)$ vibrations is illustrated in Figure 8 taking as an example complexes of pentachlorophenol with amines [26]. In the infra-red spectra the correlated quantity is the center of gravity of protonic vibrations (ν_{cg}) versus the ΔpK_N value. Figure 9 represents numerous data related to ν_{cg} collected for various O–H···N hydrogen bridges [27]. The scattering of experimental points is very large that seems to be understandable taking into account various experimental conditions and differences in the acid-base interaction for various components. One of the reasons of scattering is a difficulty connected with precise assessment of the position of broad bands. As follows from the results collected by Albrecht and Zundel [28] for the complexes of phenols with octylamine, the maximal absorbance in the range of continuous absorption corresponds to 50% of proton transfer that is shown in Figure 10.

3. Electronic Spectra and the Proton Transfer Degree

The UV-Vis spectroscopy is a very useful method of studies on the proton transfer degree in the Brönsted acid-base

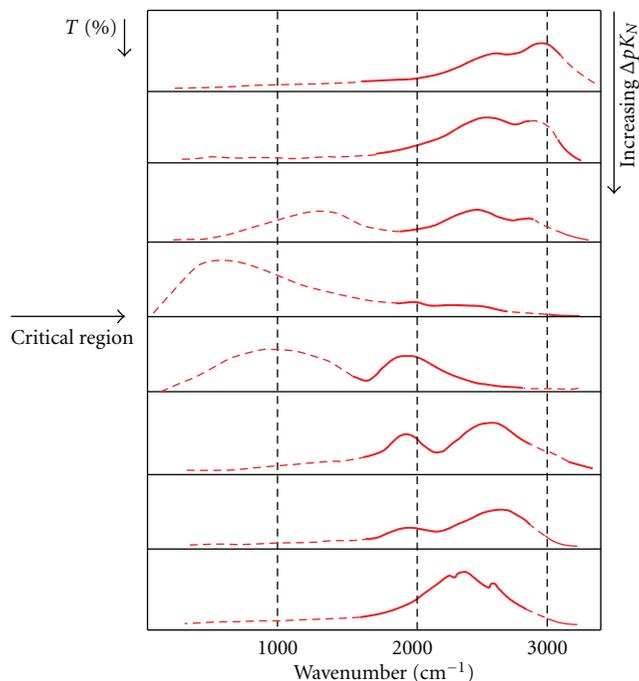


FIGURE 8: The evolution of infra-red absorption ascribed to $\nu(\text{OH})$ when increasing ΔpK_N for complexes of pentachlorophenol with amines [26].

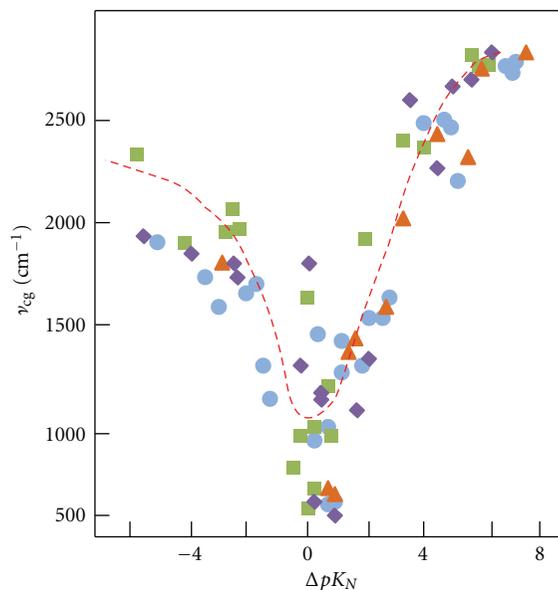


FIGURE 9: The center of gravity ν_{cg} for protonic vibrations as a function of ΔpK_N for various complexes of carboxylic acids [27].

system for the diluted solutions. The majority of quantitative data related to the proton transfer equilibria relates mainly to the complexes between phenols and amines [24, 29–35]. In the UV spectra, the tautomeric equilibrium is characterized by appearance of a new band corresponding to the $\pi \rightarrow \pi^*$ transition in the phenolate ion. After careful quantitative separation of the HB and PT bands the proton transfer equilibrium $c_{\text{PT}}/c_{\text{HB}}$ can be evaluated. As an example of the UV spectra with the proton transfer equilibrium, we use

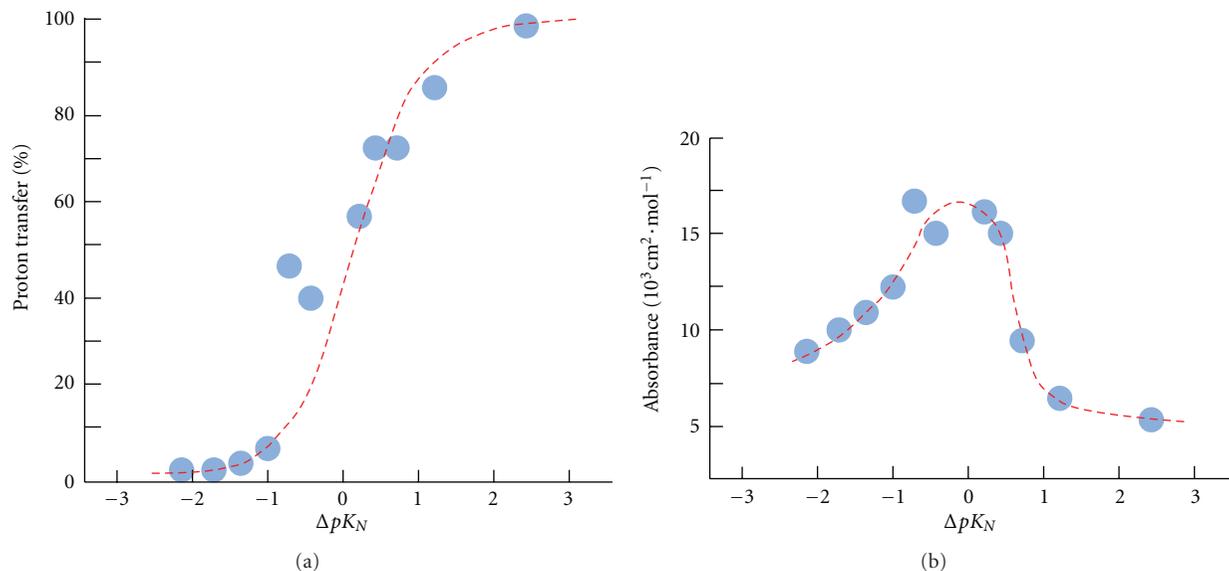


FIGURE 10: The proton transfer degree (a) and intensity of continuous absorption (b) for complexes of phenols with octylamine [28].

the system of 2,4,6-trichlorophenol in tributylamine (TBA) [29] presented in Figure 11 which shows the overlapping of HP and PT bands. From the equilibrium constant, other thermodynamic parameters can be determined according to equation:

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}, \quad (7)$$

where K is calculated by using intensities of bands and molar absorption coefficients of corresponding forms:

$$K = \left(\frac{I_{PT}}{I_{HB}} \right) \left(\frac{\epsilon_{HB}}{\epsilon_{PT}} \right). \quad (8)$$

The first quantitative studies by using the electronic absorption spectra were performed by Baba et al. [30] for complex of 4-nitrophenol with triethylamine in 1,2-dichloroethane who found $\Delta H^\circ = -13 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta S^\circ = -49.8 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. Similarly, Crooks and Robinson [31] investigated complexes of bromophenol with methyl derivatives of pyridine in chlorobenzene. The obtained data correspond to $-\Delta H^\circ$ in the range 12–38 $\text{kJ}\cdot\text{mol}^{-1}$ and $-\Delta S^\circ$ in the range 29–55 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The values of thermodynamic parameters for the complexes of chlorophenols with TBA [29] are comparable with those of nitrophenol.

From the studies [29, 37–44] it follows that the concentration of the PT form, independently of the H-bonding type, increases with an increase of ΔpK_a value of interacting components, as well as with increase of the solvent activity and the drop of temperature.

For the systems with negative or close to zero ΔpK_a values, it was not possible to find traces of the PT band even in the most active solvents at temperatures as low as below -190°C [38]. Thus, for observation in UV spectrum participation of the PT form even in favorable conditions (low temperature and high polarity of solvent), some boundary ΔpK_a value is necessary.

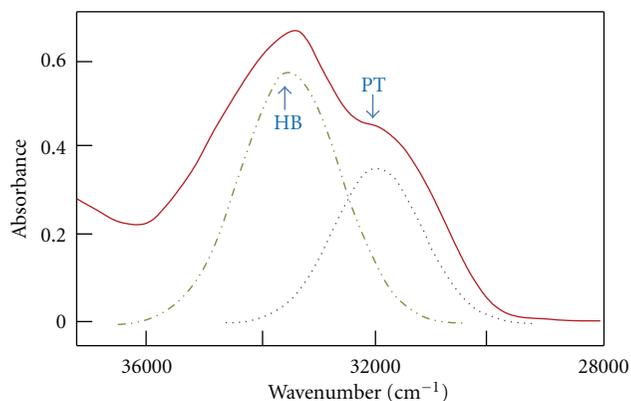


FIGURE 11: The plot of the absorbance versus wavenumber for 2,4,6-trichlorophenol in tributylamine at room temperature, $c = 5 \cdot 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$; $d = 5 \text{ mm}$.

Figure 12 shows the UV spectra for the series of complexes formed by TBA with various chlorophenols of increasing acidity. It can be seen that 2,4-dichlorophenol and 2,4,5-trichlorophenol do not show any contributions of PT species, only 2,6-dichlorophenol shows traces of the ionic PT form. For 2,4,6-trichlorophenol, a considerable amount (ca. 25%) of the PT form was estimated from the UV spectrum. Pentachlorophenol appears entirely in the zwitterionic state, whereas in a case of 2,6-dichloro- and 2,4,5-trichloro derivatives, characterized by almost the same ΔpK_a values, some contribution of the PT state shows only the former one. The ΔpK_a value is not, however, a completely satisfactory measure of the proton donor-acceptor properties in nonaqueous media.

In several papers, for example, [45–48] one considers the attention that one should apply another scale of proton donor and acceptor properties for defining the proton

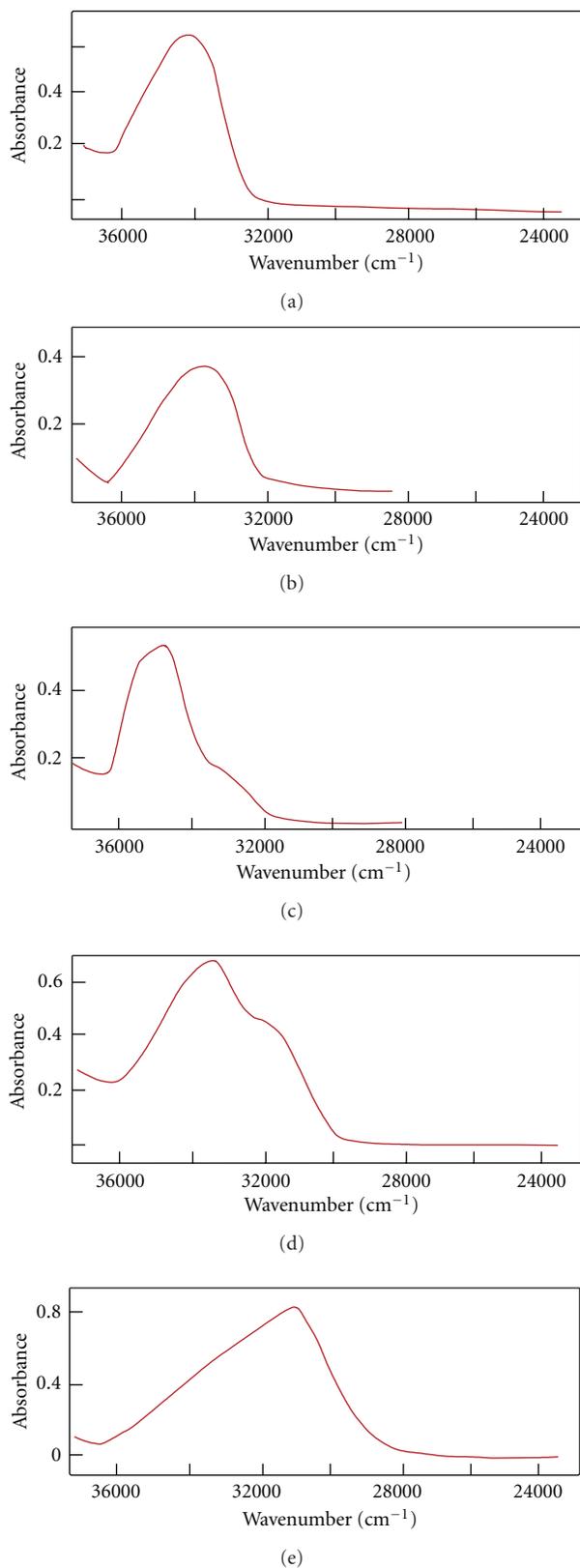


FIGURE 12: UV spectra of chlorophenols: (a) 2,4-dichlorophenol, (b) 2,4,5-trichlorophenol, (c) 2,6-dichlorophenol, (d) 2,4,6-trichlorophenol, (e) pentachlorophenol in TBA at room temperature, $c = 5 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$; $d = 5 \text{ mm}$ [29].

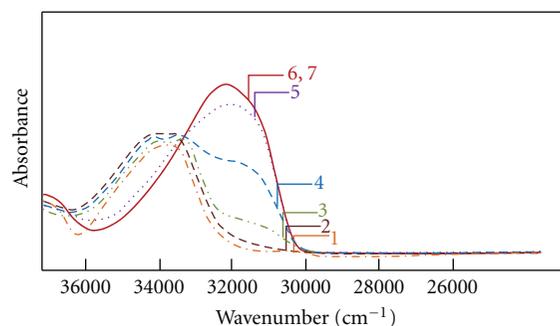


FIGURE 13: UV spectra of 2,4-dichlorophenol in TBA as a function of temperature: 298 K (1), 223 K (2), 203 K (3), 186 K (4), 165 K (5), 143 K (6), 128 K (7). $C = 4 \times 10^{-4} \text{ mol dm}^{-3}$, $d = 5 \text{ mm}$, wavenumber of PT form $\cong 32160 \text{ cm}^{-1}$ and HB form $\cong 33840 \text{ cm}^{-1}$ [29].

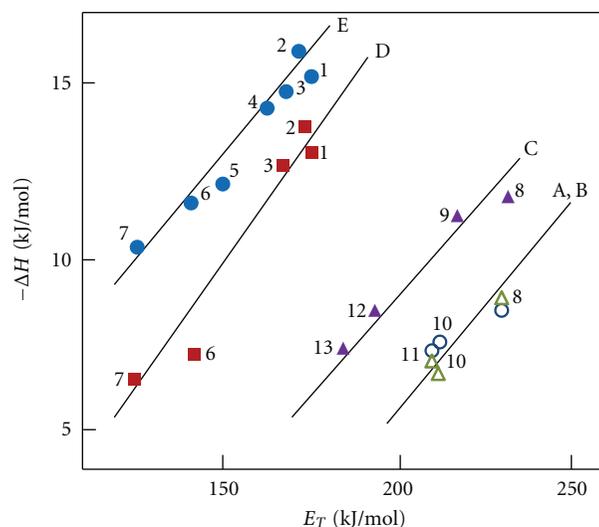


FIGURE 14: Comparison of the $\Delta H_{\text{PT}}^{\circ}$ with E_T parameters for Mannich bases: (A) 2-(N,N-dimethylaminomethyl)-4,6-dibromophenol, (B) 2-(N,N-diethylaminomethyl)-4-nitrophenol, (C) 2-(N,N-diethylaminomethyl)-3,4,6-trichlorophenol, (D) 2-(N,N-diethylaminomethyl)-3,4,5,6-tetrachlorophenol, (E) 2-(N,N-diethylaminomethyl)-4-nitronaphthol-1, in 1,2-dichloroethane (1), dichloromethane (2), n-butylchloride (3), chloroform (4), 1,4-dioxane (5), isopropylbenzene (6) squalane (7), methanol (8), ethanol (9), butan-1-ol (10), propan-1-ol (11), acetonitrile (12), and N,N-dimethylformamide (13) [36].

position in hydrogen-bonded complexes. In the analysis, one takes into account the proton affinity and deprotonation enthalpy based on calculations by using DFT methods. However, in the present article, we limited our considerations to experimental methods leading to evaluation of the pK_a values.

A strong influence of cooling on the increase of concentration of the PT form indicates on negative change of enthalpy effect on the proton transfer process. In Figure 13, the UV spectra of 2,4-dichlorophenol in TBA are shown as a function of temperature [29]. The 2,4-dichlorophenol—TBA system at room temperature does not show any

contribution of the PT state. Similar to other systems of this type, we observe a very strong influence of cooling on the contribution of the PT state. At the temperatures 203, 186, and 165 K, the values of K_{PT} are 0.33, 0.82, and 5.70, respectively. The complete proton-transfer state is reached at about 143 K and further cooling does not affect the intensity of the phenolate band.

By using electronic spectroscopy in the UV range, the PT equilibrium constants have been measured as a function of temperature in various solvents for various H-bonded systems. They allowed to determine the thermodynamic parameters of the PT process and correlate with various empirical parameters of the solvent activity. The results for Mannich bases [36, 39, 40] correlated with the Dimroth-Reichardt E_T parameter [49, 50] are presented in Figure 14. These correlations present individual straight lines with similar slope for particular Mannich bases. Such clear differentiation shows that the differences in the proton affinity of particular acid-base centers contribute essentially to the stabilization of both forms. The observed effect of solvent activity shows that the proton transfer process is characterized by two factors. Simultaneously, with previous ΔpK_a effect that can be classified as inter one, an additional factor, called an external, takes place, which correlates with the solvent activity expressed by the E_T parameter. Formally, one can express

$$\Delta H_{PT}^{\circ} = \Delta H_{int}^{\circ}(\Delta pK_a) + \Delta H_{ext}^{\circ}(E_T), \quad (9)$$

however, quantitative estimation of both components is not an easy task.

The attempt has been undertaken to correlate the ΔH_{PT}° values with other parameters characterized the solvent activity, but the best correlation was obtained with E_T . Thus, the external factor contains two effects, that is, the electrostatic stabilization of the ionic form and the donor-acceptor interaction of solvent molecules with the free electron pair of the phenolate oxygen atom. So far, no proton transfer equilibrium was observed in the gas phase that proves decisive role of the solvent for observation of the proton transfer. This is confirmed by relatively high values of entropy effect, ΔS_{PT}° from -30 up to $-70 \text{ J K}^{-1} \text{ mol}^{-1}$ [36, 39, 40] that confirms a considerable redistribution of molecules and high increase of ordering of solvent molecules under influence of intramolecular proton transfer.

The UV spectra were used to locate the position of 50% proton transfer in chloranilic acid-amine complexes; the similar result was deduced from IR and NMR studies [51]. Chranina et al. [52] studied the proton transfer equilibria between hydroxyanthraquinone dyes and aliphatic amines in low-polarity solvents by UV spectroscopy. The shift of this equilibrium in an external electrical field has been observed by the method of electrochromism in the visible region. Also, the mechanism of proton transfer reactions between various acids and amines was studied kinetically by applying UV spectroscopy, when the order and the isotopic ratio effect were discussed [53, 54].

4. Vibrational Polarization of Hydrogen Bonded Systems

It has been broadly postulated by Zundel [55] that for the characteristic dependences of the important physical parameters on ΔpK_N , with the anomalous behavior in the critical region, the large proton polarizability of the hydrogen bonds is responsible. The extraordinary increase in proton polarizability with increased strength of the hydrogen bonds in heteroconjugated systems was the aim of detailed infrared studies conducted by Hawranek's group. For six systems of pentachlorophenol (PCPh) dissolved in different basis, the molar vibrational polarization (P^{vib} , called also atomic polarization as it arises from atomic motions) and molar electronic polarization were determined according to the procedure sketched below. Names of the basis are given in Table 1. The PCPh-base complexes were studied in binary solutions, that is, the proton donor (PCPh) was directly dissolved in an excess of the proton acceptor. Such conditions facilitated accurate determination of optical quantities necessary for calculations of the P^{vib} values, according to the following scheme.

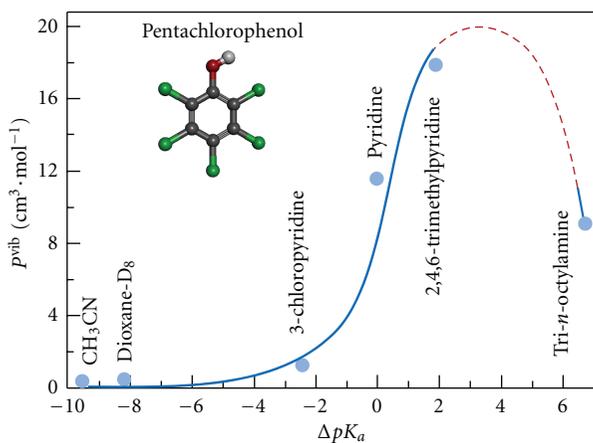
Table 1 shows the P_2^{vib} values along with the position (ν_{max}) and the half width ($\Delta\nu_{1/2}$) of the $\nu_s(\text{OH})$ band. The spectral parameters were obtained only for H-bonded systems related to the nonproton-transfer state, their values cannot be estimated with a sufficient accuracy for systems corresponding to other two states (see Figure 2). The plot of the P_2^{vib} values versus ΔpK_a , shown in Figure 15, possess the delta type character with a maximum.

It has to be mentioned here that the measurements in binary system have many advantages that facilitate the used procedure of determination of the molar vibrational polarization. However, there is also one disadvantage: the P^{vib} values are obtained for H-bonded systems differently polarized by their environment. The PCPh-base complexes are immersed in various media that have different macroscopic parameters and more or less strongly polarize the hydrogen bonds. For each system, the ξ and ΔpK_a (crit) parameters should be determined whenever the ΔpK_a values are subjected to the normalization procedure. Due to the lack of such data, the P^{vib} values on Figure 15 are plotted against ΔpK_a parameter. We can guess that the normalization and the different influence of solvents on the vibrational polarization should not meaningfully change the delta-type relation between P^{vib} and strength of the hydrogen-bonded systems.

According to Table 1, the molar vibrational polarization increases from a very small value for TmPh in inert CCl_4 solution, to a slightly larger for the OH group involved in a weak $\text{OH} \cdots \text{Cl}$ intramolecular hydrogen bond in PCPh. Noticeable increase is observed for OH group engaged in a weak intermolecular hydrogen bonds in the PCPh- CH_3CN and PCPh-dioxane systems. Their P^{vib} values compared with that for the 2,4,6-TmPh- CCl_4 indicate on the 17- and 20-fold increase. The changes are strictly correlated with the typical spectral features of H-bond formation, that is, the shift of $\nu_s(\text{OH})$ bands towards lower frequencies and the increase in its bandwidth. In relation to the system with intramolecular

TABLE 1: Spectral parameters related to the $\nu_s(\text{OH})$ band and P^{vib} of the H-bond complexes of PCPh.

| Acceptor | ν_{max} (cm^{-1}) | $\Delta\nu_{1/2}$ (cm^{-1}) | P^{vib} ($\text{cm}^3 \text{mol}^{-1}$) | Reference |
|----------------------------|---|--|--|-----------|
| CCl_4 | 3525 | 21.6 | 0.048 | [56] |
| CH_3CN | 3322 | 275.5 | 0.294 | [57] |
| Dioxane- D_8 | 3162 | 316.5 | 0.333 | [58] |
| 3-Chloropyridine | 2737 | 945 | 1.182 | [59] |
| Pyridine | — | — | 12.5 | [60] |
| 2,4,6-Trimethylpyridine | — | — | 17.8 | [61] |
| Tri- <i>n</i> -octylamine | — | — | 9.0 | [62] |
| 2,4,6-TMPH- CCl_4 | 3622 | — | 0.017 | [56] |

FIGURE 15: P^{vib} plotted versus ΔpK_a of complexes formed by PCPh with various proton acceptors.

hydrogen bonds (PCPh- CCl_4), the increase is 6-fold for the PCPh- CH_3CN and 7-fold for the PCPh-dioxane complex. It reveals that formation even rather weak intermolecular H-bond, when the proton is located in a relatively narrow single-minimum proton potential near the acid (Figure 1 (1)), leads to a drastic increase in P^{vib} of the OH group.

The PCPh-3-chloropyridine system, with still relatively asymmetrical hydrogen bond, is close to a border between the HB and the PT equilibrium states (see Figure 2). However, its P^{vib} value, compared with that obtained for the system with intramolecular H-bonded, shows almost 25- and 70-fold increase in comparison with the free OH-group in the 2,4,6-TMPH- CCl_4 system. Despite this, the molar vibrational polarization of the PCPh-3-chloropyridine system is still markedly less than its molar electronic polarization.

The complex of PCPh with pyridine with symmetrical $\text{O} \cdots \text{H} \cdots \text{N}$ hydrogen bond is classified to the proton transfer state. The molar vibrational polarization of the OH group rises to $12.5 \text{ cm}^3 \cdot \text{mol}^{-1}$. This value compared with that obtained for free (2,4,6-TMPH- CCl_4) and for the intramolecularly bonded (PCPh- CCl_4) OH group shows almost 600- and 200-fold increase, respectively.

According to [28], the complex of PCPh with 2,4,5-trimethylpyridine is close to the border between the PT equilibrium and the PT states. Its molar vibrational polarization is more than 370 and 1000 times higher than in

the PCPh- CCl_4 and 2,4,6-TMPH- CCl_4 system, respectively. For the PCPh-2,4,6-trimethylpyridine complex hydrogen bond possess largest proton polarizability. The last complex of PCPh with tri-*n*-octylamine belongs to the PT state. According to Figure 15, its P^{vib} value drops almost twice when compared with the previous system. For such large change of P^{vib} , a characteristic evolution of the infrared spectra corresponding to the PT state, shown in Figure 8, is responsible.

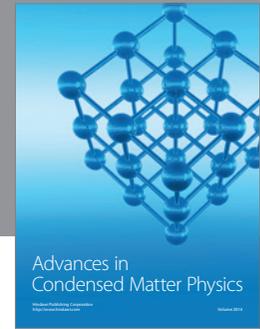
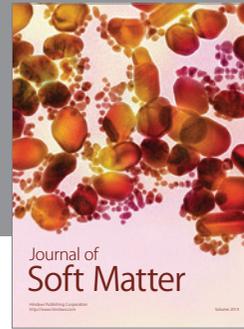
Summing up, the very large P^{vib} values determined for PCPh complexes with pyridine and 3-chloropyridine are excellent confirmation of the extraordinary properties of hydrogen bonds from the transition region with symmetrical potential. Moreover, they confirm very well Zundel's concept that an extreme broadening of the OH band occurs for hydrogen bonds showing the largest proton polarizability [55].

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