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Critical Behavior Studies of 2,4-Dichlorobenzoic Acid – Amines Hydrogen-Bonded Complexes Utilizing Fourier-Transform Infrared Spectroscopy

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A series of crystalline 1:1 hydrogen-bonded complexes between 2,4-dichlorobenzoic acid (DCBA) and various quinolines and pyridines was prepared. Fourier-transform infrared spectra (FTIR) of these complexes are presented and analyzed in the ν_{OH} and $\nu_{C=O}$ regions. The correlation between the gravity center of the protonic vibrations ν_{cg} (cm^{-1}), the quantity $\Delta\nu/\Delta\nu_0$ and the pK_a values of the amines are presented. The integrated intensities in solution A ($Lmol^{-1}cm^{-2}$) and in the crystalline state A ($kg\,mol^{-1}\,cm^{-2}$) in the $\nu_{C=O}$ region were correlated with the pK_a values of the investigated amines. Striking anomalies are observed at the critical region (50% proton transfer). These results can be interpreted by assuming that quasi-symmetrical O..H..N bridge is formed with a single, flat minimum potential in the solid state and a double minimum potential in solution.

Key words: hydrogen bond , IR spectra, critical behavior

Hydrogen bonding occupies a prominent position in modern chemistry. It is fundamental for molecular recognition and supramolecular synthesis and hold a central role in biology [1–5]. The prediction of the properties of hydrogen bonding is one of the most important problems in science especially such properties in the critical region. There are more data available proving that by varying the donor-acceptor capability of the interacting components, a critical region can be reached intermediate between the non-proton transfer (HB) and the proton transfer (PT) states. The critical region is characterized by a number of anomalies such as very low values of the IR frequency of the protonic bands with the formation of a continuous absorption called continua [6–10], stepwise increase of the polarity expressed by the dipole moment [11] or nuclear quadrupole moment resonance frequency [12–14] and maximum value of the proton magnetic resonance frequency [15–17]. Crystallographic data indicated that hydrogen bonds from such a critical region are the shortest ones [18–20]. Based on the IR data for the HX complexes in argon matrices, the critical region is characterized by high values of isotopic ratio [21,22].

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More questionable seems to be the interpretation of the IR spectra of hydrogen bonded complexes in the solid state. Thus, the evolution of IR spectra is to a large extent similar to that observed in solution. The critical point is naturally shifted to lower pK_a values because the solid state favors the PT polar state. On the other hand, it is difficult to expect double minimum potential function of proton motion to be present in the solid HB complexes. Therefore, it seems justified to carry out further IR studies of hydrogen-bonded complexes in the solid state and in solution in polar and non polar solvents to shade more lights about the behavior of the critical region complexes.

Consequently, the aim of the current contribution was to prepare and study the Fourier-transform infrared spectra of DCBA – amines hydrogen bonded complexes. This acid is a strong enough, pK = 2.68 to form a variety of complexes starting from non polar, relatively weak complexes and ending with proton transfer complexes. Another important aim of this work was the presentation of the correlations between the gravity center of the protonic vibrations as well as the integrated intensities in different regions and the pK_a values of the amines. This correlations will present more information about the different anomalies in the behavior of the complexes belonging to the critical region.

EXPERIMENTAL

DCBA was of Fluka spectroscopic grade. The pyridines and quinolines were Aldrich and Merck products. The solid complexes of DCBA with pyridines and quinolines were precipitated from equimolar solutions of the components in acetonitrile. The composition of the complexes was determined on the basis of C, H, N elemental analysis, which provided that 1:1 complexes were formed. The FTIR spectra were measured on a Perkin–Elmer paragon 1000 spectrophotometer using KBr pellets, which is oven dried at 140°C. The weight of KBr was 0.3 gram and that of the complex was adjusted to give a molality that ranged from 0.015 to 0.02 molal. A Mettler 21 balance was used for weighting. The thickness of KBr pellets ranged from 0.08 to 0.085 cm. The complex was very well mixed and ground with KBr, and the preparation of the pellet was repeated three times for each complex and the results were averaged. The thickness of the cell used for solution spectra was 0.015 cm.

Methods of calculations

The center of gravity of the protonic vibrations and the integrated intensities were estimated as described previously [23,24]. The quantity $\Delta\nu/\Delta\nu_0$ was estimated using Rumon and Johnson equation [19].

$$\Delta\nu/\Delta\nu_0 = (\nu_{C=O} - \nu_{C=O})/(\nu_{C=O} - \nu^{as}_{COO^-})$$

dimer acid 1695 cm^{-1} adduct dimer acid sodium salt 1589 cm^{-1}

The base line was corrected as described in [23].

RESULTS AND DISCUSSION

The FTIR spectra of different complexes, representing the three regions of hydrogen bonding, are shown in Figure 1. Figure 1a presents the FTIR spectrum of DCBA, where a broad band extending from 3100 to 2500 cm^{-1}, representing the OH stretching vibration, has been recorded. Figure 1b presents the FTIR spectrum of the molecular complex DCBA-6-nitroquinoline, which resembles that of DCBA in the OH stretching region, where a broad less intense stretching vibration band of the OH group involving in intermolecular hydrogen bonding with DCBA (OH….N), appeared. DCBA-quinoline complex, Figure 1c, is another example of the molecular complexes showing another feature including the appearance of two broad bands with low intensities at 1990 and 2400 cm^{-1}, respectively, representing the $\nu_{OH...N}$ vibration band. Figure 1d shows the FTIR spectrum of DCBA-3-methylisoquinoline complex as an example of the critical region complexes. It is clearly observed that the spectrum is quite different from those of the molecular complexes. The most important feature in it is the broadening of the protonic band, the absorption extends over almost the entire IR region producing continua extending from 4000 to 400 cm^{-1}. The strongly anharmonic potential, which can be anticipated from complexes in the critical region, causes coupling of the protonic vibration with the internal vibration of the complex components, giving rise to the occurrence of sharp Evans holes down to 1000 cm^{-1}. Another interesting feature in the critical region complexes is the weak absorption in the region 2500–2000 cm^{-1} or its complete disappearance. Figure 1e presents an example of the proton transfer region complexes DCBA-2,4,6-trimethylpyridine. The absorption peak that appeared at 2675 cm^{-1} could be assigned to ν^{+}_{NH}, on the other hand, the collidinium ring vibration could be detected superimposed on the broad $\nu^{as}_{COO^-}$ at 1634 cm^{-1} confirming the proton transfer process in this complex. Another example of the proton transfer complexes is shown in Figure 1f for DCBA-o-methylaminopyridine. This amine contains two basic nitrogen centers [25], the amino group nitrogen (pKa = 8.79) and the pyridine ring nitrogen (pKa = 2.04). The presence of the methylene group in this amine inhibits the resonance conjugation between the amino group and the pyridine ring producing higher electron density on the amino nitrogen. Consequently, protonation takes place on the amino group nitrogen as confirmed by the appearance of a broad band near 3000 cm^{-1}, which could be assigned to $\nu^{+}_{NH_3}$ overlapping with the methylene stretching vibration modes. It is very difficult in these systems to follow the exact values of the ν_{OH} and ν^{+}_{NH}. Consequently, the gravity center of the protonic vibration bands is estimated ν_{cg} (OH) and ν_{cg} (NH^+) cm^{-1} in the FTIR region including the continua between 4000–400 cm^{-1}. In Table 1, the amines and the gravity center of the OH and NH protonic vibrations are collected. The dependence of ν_{cg} (OH, NH^+) on the pK_a of the amines is shown in Figure 2a. As clearly seen, the diagram consists of two wings, the left hand side one represents the molecular complexes, while the right hand side one represents the proton transfer ones. It is noticed that in Figure 2a and exactly at the point (pKa = 5.64, ν_{cg} = 2274 cm^{-1}) a transition state to the point (pKa = 6.65, ν_{cg} = 2263 cm^{-1}) until reaching the

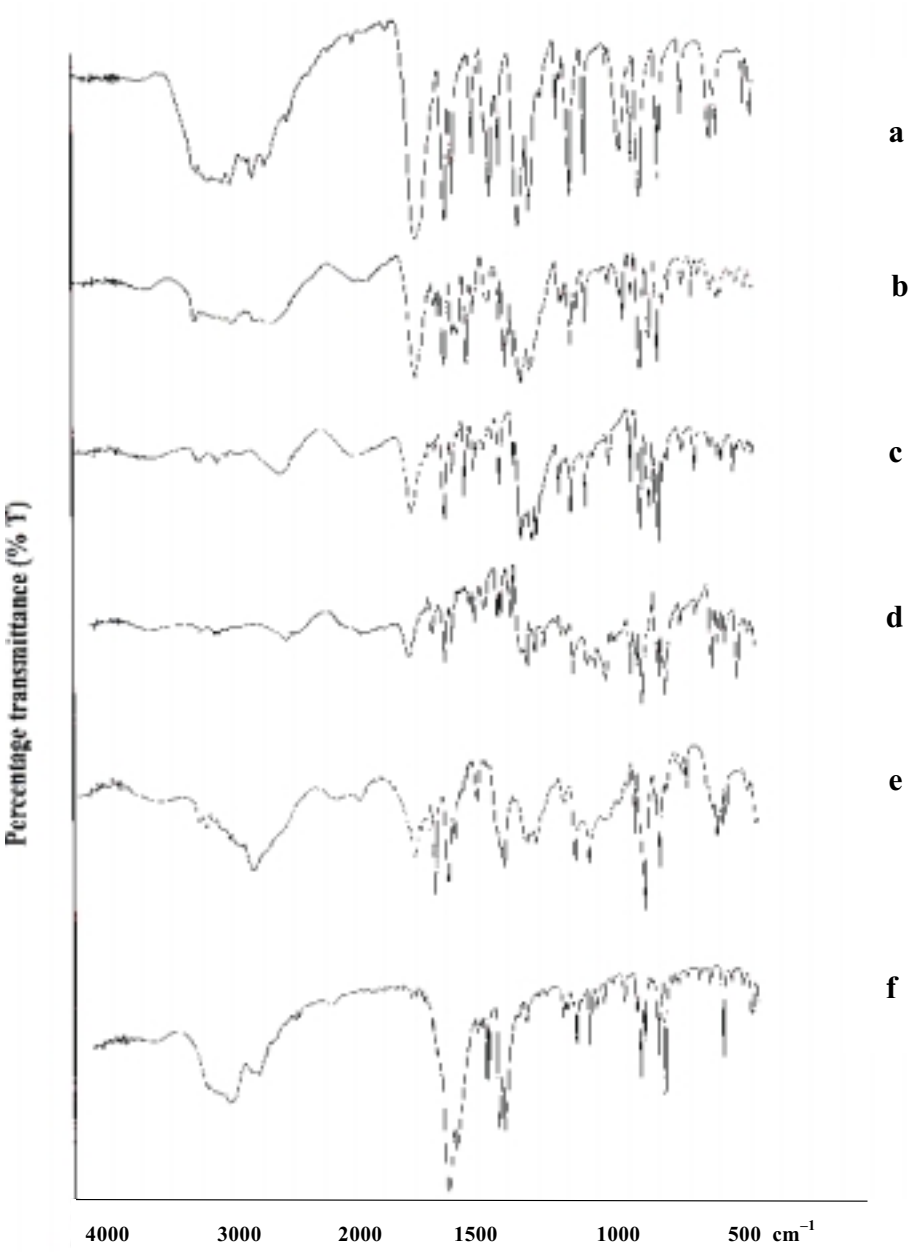

Figure 1. FTIR spectra of (a) DCBA and its hydrogen-bonded complexes with (b) 6-nitroquinoline, (c) quinoline, (d) 3-methylisoquinoline, (e) 2,4,6-trimethylpyridine and (f) o-methylamino-pyridine in the range 4000–400 cm^{-1}.

deep minimum at the point (pKa = 7.29, ν_{cg} = 2094 cm^{-1}), after which the proton transfer zone starts from the complex DCBA-2,4,6-trimethylpyridine. Hence, four complexes represent the critical region in the system under investigation having the pK_a values: 5.64, 5.65, 6.85 and 7.29. A deep minimum at pK_a equal 7.29 represents

the critical point, which is higher compared with other strong hydrogen-bonded systems results reported in [6,14]. The difference could be ascribed to the steric hindrance of the investigated quinoline complexes that retarded the proton transfer process leading to a later pK_a value, 7.29. These results could be interpreted in terms of the existence of a flat single minimum potential in the systems under investigation.

Table 1. Vibrational spectral data in the crystalline form.

Amine	pK_a	$\nu_{C=O}$ cm^{-1}	$\nu^{as}_{COO^-}$ cm^{-1}	$A \cdot 10^{-4}$ $kg\ mol^{-1}$ cm^{-2}	ν_{cg} cm^{-1}	$\Delta\nu/\Delta\nu_0$
6-Nitroquinoline	2.72	1701	–	18	3390	–
Quinoline	4.93	1719	–	14	3315	–0.23
2,4-Dimethylquinoline	5.12	1685	–	12	3298	0.094
6-Methylquinoline	5.15	1709	–	8	3291	–0.13
4-Methylquinoline	5.59	1719	–	6	2782	–0.23
3-Methylisoquinoline	5.64	1722	–	14	2274	–0.25
5,6,7,8-Tetramethylquinoline	6.65	1697	–	6	2263	–0.02
2-Aminopyridine	6.85	1688	–	8	2223	0.07
2-Amino-3-methylpyridine	7.29	1665	–	10	2049	0.28
2,4,6-Trimethylpyridine	7.43	1713	1634	16	2616	–0.17
o-Methylaminopyridine	8.79	–	1583	–	–	–
4-Aminoquinoline	9.13	–	1552	19	2769	–
Piperidine	11.2	–	1589	23	2939	–

Simultaneously, with the hydrogen bonding formation, many vibration modes are perturbed, especially $\nu_{C=O}$ and ν_{C-O}, as clearly observed in Figure 1. One observes in Figure 1a which represents the FTIR spectrum of DCBA, that $\nu_{C=O}$ and ν_{C-O} appeared at 1695 and 1300 cm^{-1} respectively with higher intensities. For the molecular complex DCBA-6-nitroquinoline, Figure 1b $\nu_{C=O}$ resembles that of the free acid but with lower intensity, the same situation was recorded for the ν_{C-O} mode at 1300 cm^{-1}. At the critical region complex DCBA-3-methylisoquinoline, Figure 1d, one clearly observes the lowering of the carbonyl intensity at 1722 cm^{-1} and the ν_{C-O} mode at 1300 cm^{-1}. Passing through the proton transfer region represented by the complex DCBA-o-methylaminopyridine, Figure 1f, it is clearly observed the $\nu^{as}_{COO^-}$ vibration mode at 1583 cm^{-1} confirming the presence of the carboxylate group with a full negative charge as asserted by the absence of the ν_{C-O} mode at 1300 cm^{-1}. The appearance of 4 sharp bands at 1371, 1392, 1432, and 1449 cm^{-1} of the pyridine ring modes confirmed the protonation of the amino group nitrogen rather than the pyridine ring nitrogen [26]. Hence, upon increasing the pK_a of the investigated amines, the infrared spectrum of the complex in the carbonyl region undergoes gradual, but profound changes. At lower pK_a values (4.93–5.59), the carbonyl frequency of the acid part is intense, narrow and shifted somewhat to higher frequencies. Higher pK_a values led to

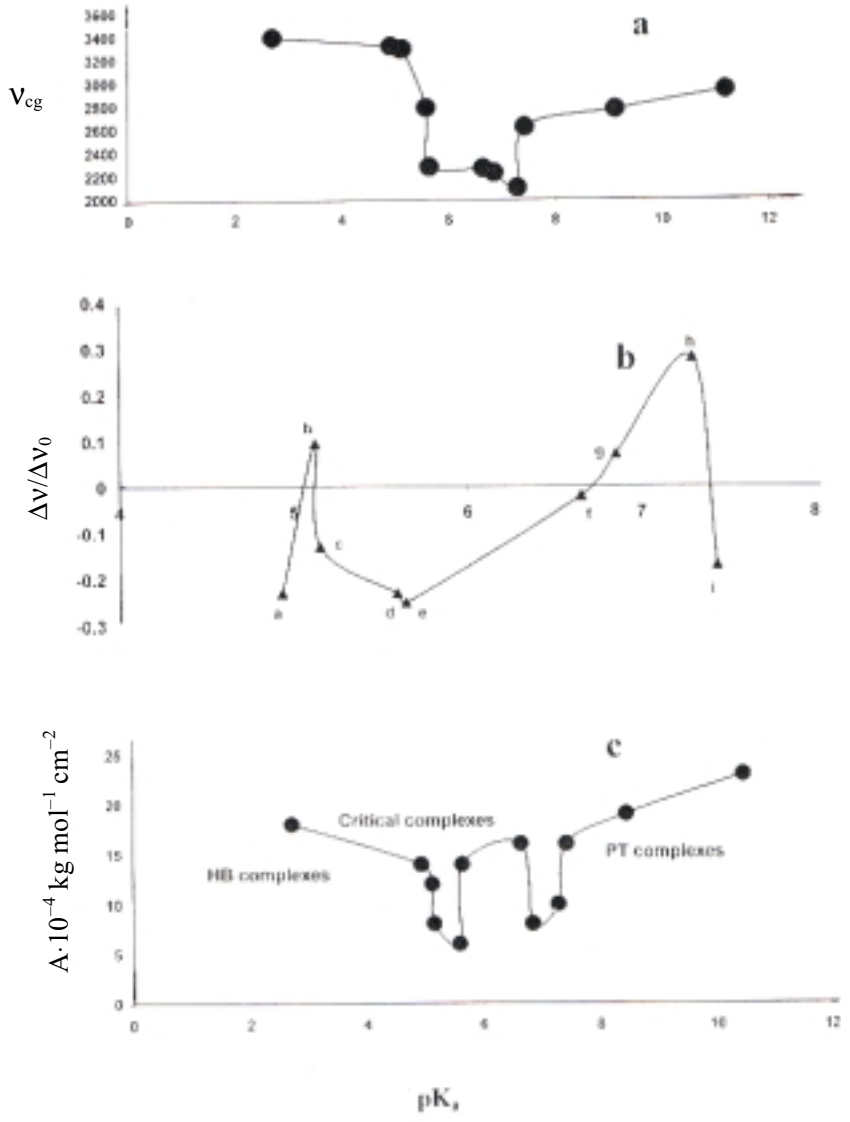

Figure 2. Correlation between (a) ν_{cg}, (b) $\Delta\nu/\Delta\nu_0$ and (c) A $\cdot10^{-4}$ kg mol^{-1} cm^{-2} and pK$_a$ of the amines.

the broadening of the $\nu_{C=O}$ and ν_{C-O} bands as a result of the strong perturbation of the carboxylic acid electronic structure. A proton transfer takes place (5.64–7.29) with increasing pK$_a$ of the amine and further increase in pK$_a$ result in the sharpening of the $\nu^{as}_{COO^-}$. A plot of the quantity $\Delta\nu/\Delta\nu_0$, which is a good measure of the degree of proton

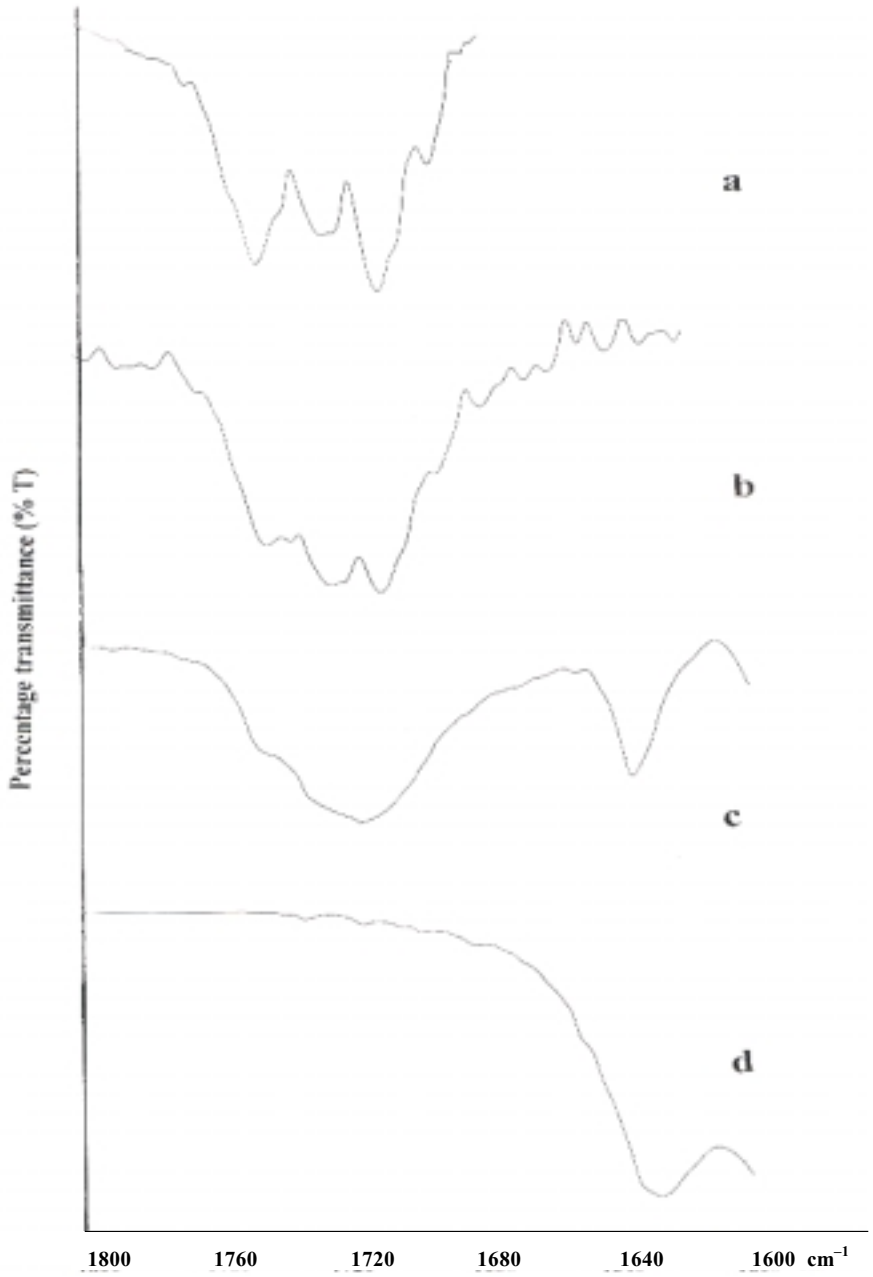

Figure 3. FTIR spectra of hydrogen-bonded complexes between DCBA and (a) 6-nitroquinoline, (b) quinoline, (c) 3-methylisoquinoline and (d) piperidine in the range 1800–1600 cm^{-1} in 1,2-dichloroethane.

transfer, *vs* pK_a of the amines is shown in Figure 2b. The a, b, c, d points represent the molecular complexes of quinoline, 2,4-dimethylquinoline, 6-methylquinoline and 4-methylquinoline after which an abrupt change in the spectral properties of the com-

plexes occurs at the point e representing the DCBA-3-methylisoquinoline complex of $pK_a = 5.64$. The points e, f, g, h represent the critical region complexes. These points represent a transition state joining the molecular region complexes with the proton transfer one starting at the complex i in Figure 2b, and representing DCBA-2,4,6-trimethylpyridine adduct. One observes in Figure 2b, the disturbance of the complexes near the critical region, where both positive and negative deviations of the quantity $\Delta\nu/\Delta\nu_0$ were recorded. An attempt was made to estimate the integrated absolute intensities for the crystalline complexes in the carbonyl region in the range 1600–1800 cm^{-1} [A(kg mol^{-1} cm^{-2})], the data are gathered in Table 1. The dependence of the integrated intensity on the pK_a of the amines is presented in Figure 2c. Two plateau areas can be identified at the left hand side for the molecular complexes and at the right hand side for the proton transfer complexes. Two maximum points at $pK_a = 5.64$ and $pK_a = 6.65$ representing the critical region complexes and joining these two plateaus were detected. The critical point can be estimated from the mean pK_a values of these two maxima (6.14) a value lower than that recorded from the previous correlations. It seems that the lower pK_a value for the critical point is favored in the solid state, where the solid complexes like the proton transfer state [6].

The FTIR spectra are followed for different complexes in the carbonyl region in the non polar solvent 1,2-dichloroethane and the polar solvent acetonitrile. Figure 3 presents the FTIR spectra in 1,2-dichloroethane. Figure 3a presents the molecular complex DCBA-6-nitroquinoline, where the carbonyl band is split upon hydrogen bond formation to the submaxima at 1708, 1724 and 1744 cm^{-1}. The same behavior was recorded for DCBA-quinoline complex, Figure 3b, with lower intensity of the recorded three submaxima, where the pK_a of quinoline is higher than that of 6-nitroquinoline leading to the decrease in the carbonyl band intensity. Figure 3c shows the FTIR spectrum of the critical complex DCBA-3-methylisoquinoline, where two absorption peaks are recorded at 1715 and 1634 cm^{-1} for the carbonyl and carboxylate frequencies respectively. These results could be rationalized in terms of the existence of a double minimum potential [27–29] in solution and consequently we have the following proton transfer equilibrium:

$$\underset{\text{(I)}}{OH\ldots N} \quad K_{PT} \quad \underset{\text{(II)}}{O^{-}\ldots HN^{+}}$$

$$HB \rightleftarrows PT$$

Figure 3d presents the proton transfer complex of DCBA with piperidine, where the proton transfer equilibrium is completely shifted towards the proton transfer species II as confirmed by the appearance of only one broad vibrational band at 1627 cm^{-1} representing $\nu^{as}_{COO^-}$ band. In the polar solvent acetonitrile, the situation is different, where the equilibrium is shifted towards the proton transfer species even for the critical region complexes as shown in Figure 4. Figure 4a presents the FTIR of

DCBA-quinoline, where both bands represent the HB and the PT species recorded at 1731 and 1633 cm^{-1}, but the intensity of the PT form is more sharp than that for the HB one asserting the shift of the equilibrium towards the PT form. For DCBA-2-aminopyridine complex belonging to the critical region complexes, only one band at 1639 cm^{-1} was recorded, which could be assigned to $\nu^{as}_{COO^-}$ overlapping with the protonated pyridinium ring vibration, Figure 4b. The same situation occurred for the piperidine complex with DCBA, Figure 4c. The integrated intensities A ($Lmol^{-1}$ cm^{-2}) in both solvents in the carbonyl region were computed, the data are collected in Table 2. Figure 5 presents the dependence of the integrated intensity on the pK_a in 1,2-dichloroethane and acetonitrile, where the critical complexes reached higher A values. In 1,2-dichloroethane, Figure 5a, a maximum was found at $pK_a = 7.29$ representing the critical point. The proton transfer equilibrium is not manifested in non polar solvents retarding the appearance of the critical region. The opposite situation was recorded in the polar solvent acetonitrile, Figure 5b, where the critical point appeared early at $pK_a = 5.64$. The situation could be rationalized in terms of double minimum potential that exists in solution. The polar solvent acetonitrile enhances the bridge polarization shifting the proton transfer equilibrium towards the proton transfer species II.

Table 2. Vibrational spectral data in solution.

Amine	$\nu_{C=O}$ cm^{-1}	$\nu_{C=O}$ average cm^{-1}	Intensity (A) $Lmol^{-1}$ cm^{-2}	Conc. mol/L
	In 1,2-dichloroethane			
6-Nitroquinoline	1744, 1724, 1708	1725	9938.2	0.0045
Quinoline	1724, 1709	1724	48555.5	0.012
6-Methylquinoline	1712	1712	50978.8	0.085
4-Methylquinoline	1740, 1710	1725	83792.1	0.017
3-Methylisoquinoline	1715, 1634	1675	83538.8	0.0328
2-Aminopyridine	1677	1677	107237	0.0256
2-Amino-3-methylpyridine	1667	1667	111789.5	0.032
2,4,6-Trimethylpyridine	1714, 1635, 1621	1657	99666.66	0.0236
4-Aminopyridine	1669, 1615	1642	44021.5	0.0186
Piperidine	1627	1627	41649.3	0.0289
	In acetonitrile			
Quinoline	1731, 1633	1684	543950	0.01
4-Methylquinoline	1727, 1630	1678	812862	0.014
3-Methylisoquinoline	1725, 1632	1678	996222	0.007
2-Aminopyridine	1630	1630	902511	0.009
2-Amino-3-methylpyridine	1639	1639	869220	0.007
o-Methylaminopyridine	1640	1640	572433	0.006
Piperidine	1634	1634	493214	0.012

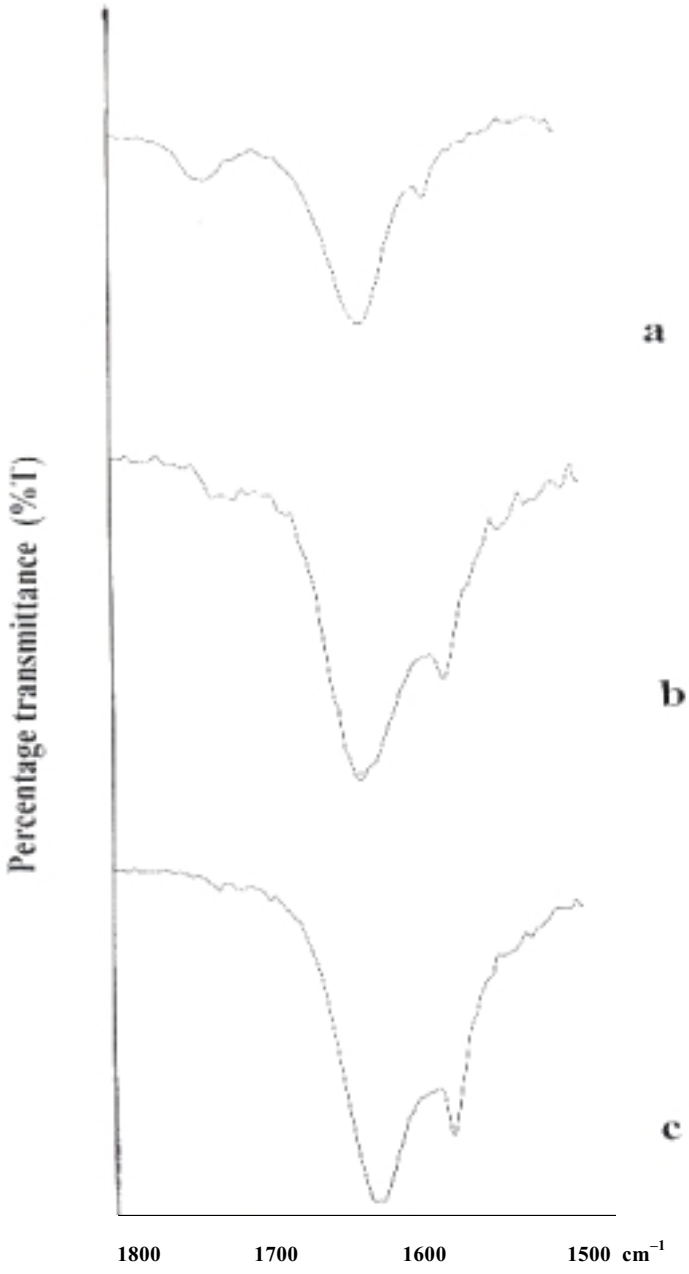

Figure 4. FTIR spectra of hydrogen-bonded complexes between DCBA and (a) quinoline, (b) 2-aminopyridine and (c) piperidine in the range 1800–1500 cm^{-1} in acetonitrile.

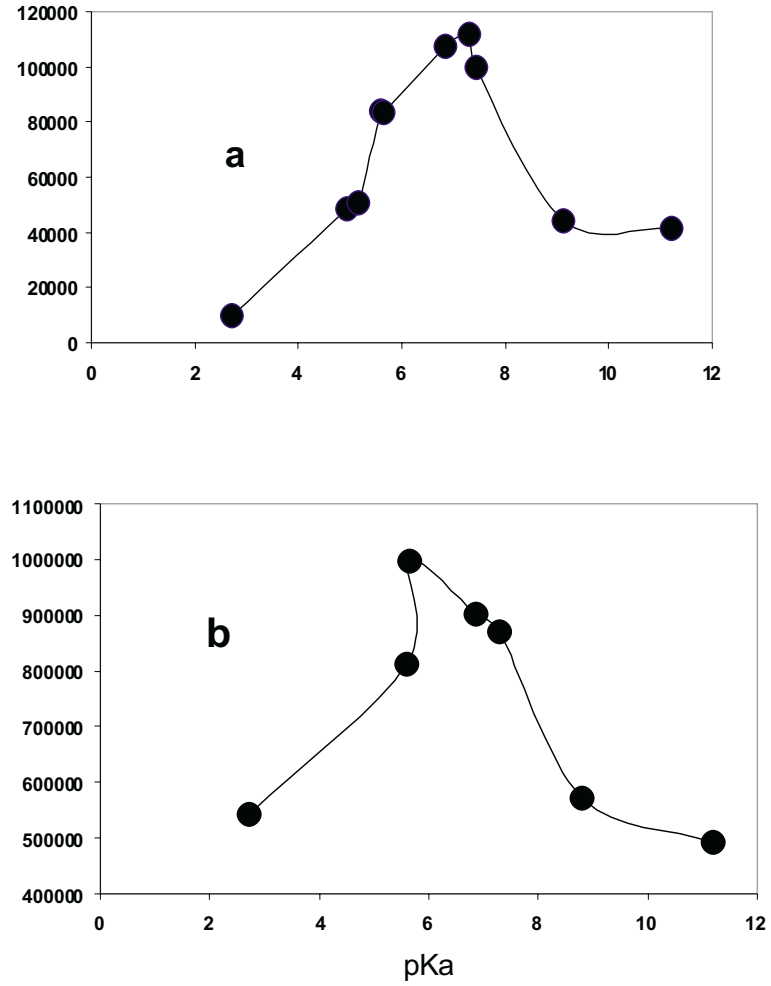

Figure 5. Correlation between A and pK_a (a) in 1,2-dichloroethane and (b) in acetonitrile.

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