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ORIGINAL ARTICLE

Spectroscopic studies of intermolecular hydrogen bonding and proton transfer complexes of chromotropic acid with some amines in methanol

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Abstract The proton transfer reactions between chromotropic acid (CTA) and some amines including benzylamine (BA), triethylamine (TEA), pyrrolidine (PY) and 1,8-bis(dimethylamino) naphthalene (DMAN) have been investigated spectrophotometrically in methanol. A long wavelength band at 365 nm has been recorded due to the proton transfer (PT) complex formation. The proton transfer equilibrium constants K_{PT} were estimated utilizing the minimum–maximum absorbances method. It has been found that K_{PT} were not depend on the amine p*K*a values, but strongly depend on the formed structures of the PT complexes. Job̓s method of continuous variations and photometric titrations were applied to identify the compositions of the formed PT complexes where 1:1 complexes (proton donor: proton acceptor) were produced. Due to the rapidity and simplicity of the proton transfer reactions and the stability of the formed complexes, a rapid and accurate spectrophotometric method for the determination of CTA was proposed for the first time.

1. Introduction

Several physical properties of H-bonded complexes, e.g. excess of dipole moment ($\Delta\mu$), change of ^{1}H, ^{13}C, ^{15}N chemical shifts ($\Delta\delta$), ^{35}Cl NQR frequency and center of gravity of the broad protonic absorption band (ν_{cg}) when plotted against Δp*K*a [p*K*a (BH^{+})-p*K*a (AH)], a sigmoidal titration curves are obtained which are usually treated as evidence of the proton transfer equilibrium (Schuster et al., 1976; Ratajczak and Orville-Thomas, 1980; Dega-Szafran and Sokolowska, 2001; Kalenik et al., 1989; Habeeb, 1997). This equilibrium depends

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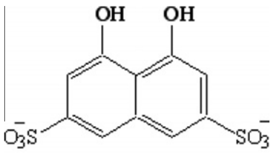
on the properties of the proton donor, proton acceptor and solvent polarity as shown below (Habeeb and Kharaba, 2003; Habeeb and Gohar, 2002).

$$\mathrm{OH}\underset{\mathrm{HB}}{\cdots\cdots}\mathrm{N} \rightleftharpoons \mathrm{O}^{-}\underset{\mathrm{PT}}{\cdots\cdots}\mathrm{H}^{+}\mathrm{N}$$

Proton transfer is one of the most important elementary reactions in chemistry and biochemistry (Deechongkit et al., 2004). They play an important role in various chemical and biological processes like stabilizing biomolecular structures (Lopez et al., 2006), controlling the speed of the enzymatic reactions (Senes et al., 2006) and constructing supramolecular structures (Parker et al., 2006). Chromotropic acid (disodium salt, $C_{10}H_6O_8S_2Na_2$, $2H_2O$), Formula 1, is a fluorogenic compound and well known as a bidentate ligand used for spectrophotometric determination of many metal ions (Kika and Themelis, 2007; Destandau et al., 2004; Hashemi et al., 2005). It has been also used for determination of nitrate (Takayanagi and Dasgupta, 2005), ozone in water (Berg et al., 1985) and for colorimetric determination of formaldehyde in air (Pretto et al., 2002). CTA belongs to aromatic sulphonic acids which are extensively used as intermediates in the production of synthetic dyes, optical brighteners and fluorescent whitening agent (Lieu et al., 1969).



Chromotropic acid
(CTA)
Formula 1

In connection with our continuing work on the proton transfer reactions of dihydroxy compounds (Habeeb and Alghanmi, 2010) and due to the above industrial applications of chromotropic acid, we now wish to report the spectrophotometric studies on the hydrogen bonding and proton transfer complexes of CTA with some amines in methanol. Based on the simplicity of the proton transfer reaction, a rapid and accurate spectrophotometric method for characterization and determination of chromotropic acid was proposed for the first time.

The composition of the formed PT-complexes was studied using Job's and molar ratio photometric titration methods. Proton transfer equilibrium constants (K_{PT}) were estimated, their physical and chemical meaning were interpreted. In addition, the solid PT complexes between CTA and BA and DMAN were isolated and characterized using elemental analysis and FTIR measurements.

2. Experimental

2.1. Apparatus

All spectrophotometric measurements were performed using a spectrophotometer (UV-1601 Shimadzu, Japan) with optional spectroscopy software version 3.7 and with silica cells of 1 cm thickness in the wavelength region 200–400 nm. The temperature gives uncertainty ±0.1 °C with a Shimadzu TCC-ZUOA temperature controller unit. The infrared spectra of the isolated solid proton transfer complexes were measured in KBr pellets with Perkin–Elmer, Spectrum RXIFTIR. Elemental analysis for C, H and N centers of the solid complexes were measured by Perkin–Elmer 2400 micro analyzer.

2.2. Chemicals

All chemicals used were of analytical grade. Chromotropic acid (CTA, $C_{10}H_6O_8S_2Na_2$. $2H_2O$, FW 400.29, mp > 300°), benzylamine (BA, C_7H_9N, FW 107.15, bp 183°), triethylamine (TEA, $C_6H_{15}N$, FW 101.19, bp 89.7°) and pyrrolidine (PY, C_4H_9N, FW 71.11, bp 87°) were supplied by (Acros organic), while 1,8-bis(*N*,*N*-dimethylamino) naphthalene (DMAN, $C_{14}H_{18}N_2$, FW 214.31, mp 47.8°) was supplied by (Fluka) and methanol was supplied by (Panreac). CTA and amines were used without further purification.

2.3. Synthesis of the solid complexes

The solid 1:1 complexes of the (CTA) with (BA) and (DMAN) were synthesized by mixing equimolar amounts of both (CTA) and (BA) or (DMAN) in methanol and the resulting complex solution was left standing overnight at room temperature. The solid complexes was separated as dark brown crystals and dried over calcium chloride for 24 h.

Elemental analysis, for (CTA–BA) $C_{17}H_{19}O_{10}NS_2Na_2$ complex, calculated: C, 40.24%, H, 2.96% and N 2.76%. Found: C, 41.25%, H, 2.73% and N 3.88%. For (CTA–DMAN) $C_{24}H_{28}O_{10}N_2S_2Na_2$ complex, calculated: C, 46.91%, H, 3.91% and N, 4.56%. Found: C, 47.26%, H, 4.06% and N, 3.85%.

2.4. Calculation of the proton transfer formation constants (K_{PT})

For the purpose of UV–Vis spectral determination of the proton transfer equilibrium constants (K_{PT}), the minimum–maximum absorbances method has been applied according to the following procedure: 1 mL of (CTA) of freshly prepared stock solution (1×10^{-3} mol L^{-1}) was transferred into a series of 10 mL calibrated flasks. To each of these were added different concentrations of the amines freshly prepared stock solution (1×10^{-3} mol L^{-1}) for PY, TEA, DMAN and (1×10^{-2} mol L^{-1}) for BA. The volume was made up to the mark with methanol.

The absorbances of the mixture solutions were recorded against methanol blank. The least concentration of the added amine leads to the minimum absorbance of the complex (A_{min}).The concentration of the amine is increased gradually and the absorbance is recorded at the absorption band of the PT-complexes (A_{mix}) until the maximum and constant absorbance of the formed PT-complexes is obtained (A_{max}). The PT formation constants (K_{PT}) are estimated by using the following equation (Habeeb and Alghanmi, 2010; Berman et al., 1978; Habeeb et al., 2001; Alattas et al., 2009).

$$A_{max} = A_{mix} + \frac{A_{mix} - A_{min}}{K_{PT} \times C_{amine}} \tag{1}$$

where A_{max}: maximum absorbance of the complex, A_{min}: minimum absorbance of the complex, A_{mix}: complex absorbances between A_{max}, A_{min} and C_{amine}: concentration of the added amine in mol L^{-1}. The results were averaged in order to extract a representative central K_{PT} value with minimum error.

3. Results and discussion

3.1. Electronic spectra

An example of the electronic absorption spectra representing the hydrogen bonding interaction between 1×10^{-4} mol L^{-1} (CTA) with different concentrations from each amine in methanol is shown in Fig. 1. The electronic spectra revealed a band lying between 350 and 400 nm attributed to the π–π^* transition of the formed PT-complexes. In addition, a gradual increase of the amine concentrations was found to increase the PT-absorbance band due to the increase in the PT complex formation.

The electronic spectra of the proton transfer reactions of CTA with the amines, Scheme 1, revealed one isosbestic point at 265 nm corresponding to the proton transfer equilibrium between CTA and amines (Scheme 2). CTA possesses two hydroxyl groups of phenolic type. Hence, it is expected that the hydrogen bonding interaction between CTA with the amines takes place through the more acidic OH one (p*K*a = 5.36) (Bardez et al., 2001).The establishment of another equilibrium including the interaction between the formed proton transfer complexes and other amine molecule does not occur. This assumption is based on the week acidity of the second phenolic OH group of CTA (p*K*a = 15.6) (Bardez et al., 2001) together with the absence of another isosbestic point in the electronic spectra in Fig. 1.

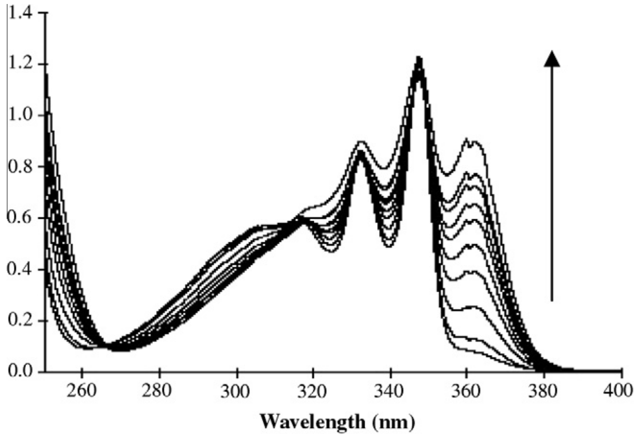
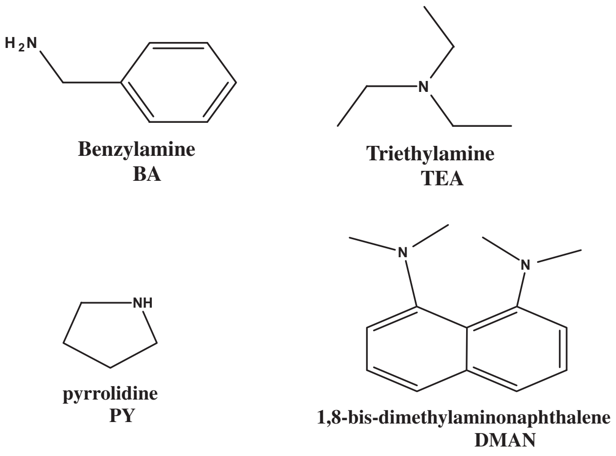


Figure 1 Electronic spectra of the proton transfer complex formation between 10^{-4} mol L^{-1} CTA and various concentrations of pyrrolidine in methanol (1) 1×10^{-5}, (2) 2.0×10^{-5}, (3) 3.0×10^{-5}, (4) 6.0×10^{-5}, (5) 9.0×10^{-5}, (6) 1.2×10^{-4}, (7) 1.5×10^{-4}, (8) 1.8×10^{-4}, (9) 2.0×10^{-4} and (10) 2.2×10^{-4} mol L^{-1}.



Scheme 1 Chemical structures of proton acceptors.

3.2. Physical and chemical meaning of K_{PT}

The formation constants of the PT-complexes were calculated using the minimum–maximum absorbances method. The p*K*a values (Habeeb and Kharaba, 2003; Perrin et al., 1965) and the concentration ranges of the amines, together with the K_{PT} values were shown in Table 1.

The K_{PT} values were interpreted as follow. Generally, K_{PT} record high values, confirming the high stability of all the formed PT-complexes. On the other hand, K_{PT} were independent on the p*K*a values of the amines but strongly depended on their structures. From results shown in Table 1, one can observe that K_{PT} for PY complex is nearly four times that for BA although they have similar p*K*a values. This situation could be rationalized in terms of higher steric hindrance of BA complex than PY one. Moreover, the intermolecular hydrogen bonding between methanol oxygen and the NH proton of secondary amines is more favored than that with primary amine protons (short range salvation effect) (Habeeb and Kharaba, 2003; Habeeb and Gohar, 2002).

This interaction shifts the electron pair of NH bond towards the nitrogen atom and hence increasing its electronic density. Consequently K_{PT} reached higher value for PY complex than BA one. In addition, Benzylamine interacts with methanol through intermolecular hydrogen bonding with the methanol OH group which leads to lowering its K_{PT}. Also, it is clearly observed from Table 1 that, K_{PT} for the complex (CTA–TEA) exhibited the highest value over the other three complexes which could be attributed to the high electron density on the nitrogen center from high inductive effect of the three ethyl groups.

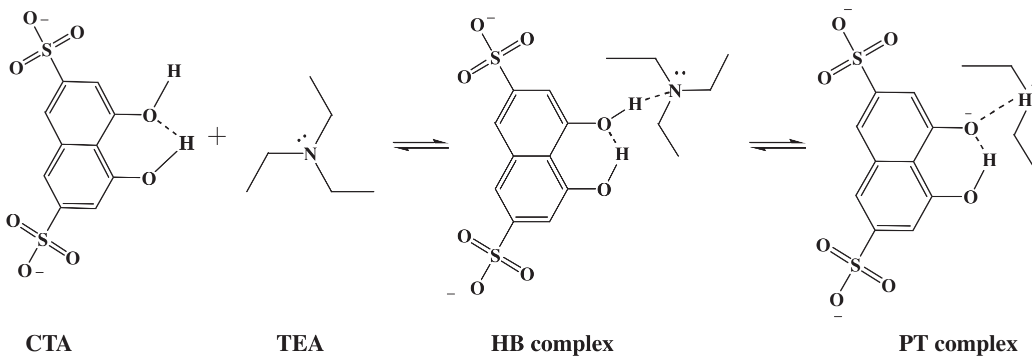
Although DMAN has higher p*K*a value than TEA, it exhibited small K_{PT} based on the higher steric hindrance of the PT complex of (CTA–DMAN) compared with TEA one. On the other hand, one cannot disregard the involvement of the two lone pair of electrons of DMAN in a resonance interaction with the naphthalene ring which reduces the electron density on the two nitrogen centers and hence K_{PT} reached low value.

3.3. Optimization of variables

Several important controlling factors in the process of proton transfer complex formation including the effect of reagent concentration, time and temperature were studied, optimized and evaluated in the following sections.

3.3.1. Effect of reagent concentrations

The effect of reagent concentrations was studied by following the absorbance of the PT-complexes between an increased amounts of 1×10^{-3} mol L^{-1} of PY, TEA and DMAN and 1×10^{-2} mol L^{-1} of BA with 1 mL of 1×10^{-3} mol L^{-1} CTA in 10 mL calibrated flasks and the volume was made up to



Scheme 2 Mechanism of the PT reaction between CTA and TEA.

Table 1 p*K*a, concentration range of amines and K_{PT} values.

Amine	p*K*a	Concentration range of amines (mol L^{-1})	$K_{PT} \times 10^{-3}$ (L mol^{-1})
BA	9.33	1×10^{-4}–3×10^{-3}	4.5
TEA	10.75	5×10^{-6}–4.5×10^{-5}	217.6
PY	11.31	1×10^{-5}–2.2×10^{-4}	14.8
DMAN	12.34	1×10^{-5}–3×10^{-4}	28.5

10 mL with methanol. It has been found that maximum and constant absorbance of the PT-complexes were obtained with 1 mL of 1×10^{-3} mol L^{-1} from PY, TEA and DMAN and 1 mL of 1×10^{-2} mol L^{-1} BA, respectively.

3.3.2. Effect of time and temperature on the PT reaction

The optimum reaction time was determined by monitoring the absorbance of the PT complexes resulting from mixing 1×10^{-4} mol L^{-1} of CTA with the optimum concentrations of each amine at room temperature (25 ± 5 °C). It has been found that maximum absorbance of the PT complex was obtained instantly for all complexes.

In addition, it has been recorded that the PT complexes of CTA were stable for 30, 75, 90 and 120 min with BA, TEA, BT and DMAN, respectively. The effect of temperature on the PT-complex formation was monitored by following the absorbance at 362 nm of the above mixtures in the temperature range 20–40 °C. The result of this study indicated that 20 °C is the optimum temperature as seen in Table 2.

3.4. Composition of the formed PT-complexes

The compositions of the formed PT-complexes between CTA and each of the studied amines were studied by applying Job's method of continuous variations (Job, 1928). An example of Job's plots is presented in Fig. 2 which indicates that the maximum absorbance was recorded at 0.5 mole fractions confirming a 1:1 PT-complex formation (CTA: amine).

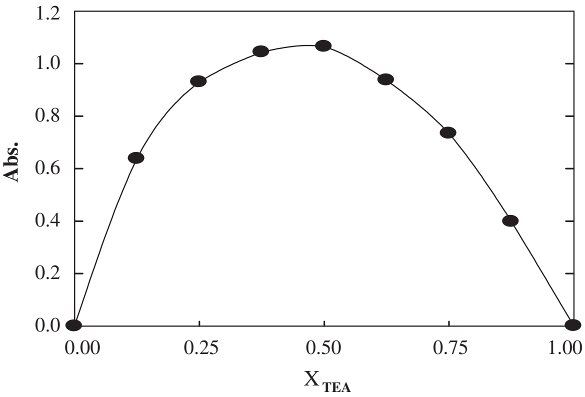


Figure 2 Continuous variation plot for the PT-complex of CTA with TEA.

Photometric titrations at 362 nm for the PT-reaction between CTA and the studied amines in methanol were also applied to study the composition of the formed PT-complexes according to the following procedure (Skoog, 1985). A constant concentration from CTA (1×10^{-4} mol L^{-1}) is mixed with variable concentrations from each amine to give amine to CTA molar ratios up to 1.5. In all the photometric titrations, the CTA to amine stoichiometric ratio was found at 1:1. An example illustrating the photometric titrations is presented in Fig. 3.

3.5. Development and validation of the analytical method

3.5.1. Calibration curves, linearity and sensitivity

Under the specified optimum reaction conditions, the calibration curves for CTA with BA, PY, TEA and DMAN, respec-

Table 2 Effect of temperature on the PT reactions.

Temp. °C↓	BA↓	↑Absorbance↓	PY↓	DMAN↓
		TEA		
20	0.487	1.774	0.547	0.511
25	0.425	1.768	0.531	0.502
30	0.400	1.759	0.521	0.502
35	0.352	1.753	0.508	0.502
40	0.337	1.747	0.498	0.506
45	0.306	1.694	0.487	0.506

tively, were constructed (Fig. 4). The regression equations for the results were derived by using the least-squares method. In all cases, Beer's law plots ($n = 6$, Fig. 4) were linear with small intercepts and good correlation coefficients (R^2) in the general concentration range of 4–40 μg mL^{-1} (Table 3).

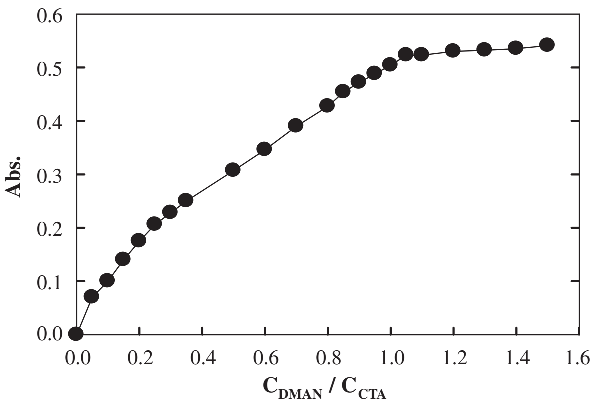


Figure 3 Photometric titration plot of CTA with DMAN.

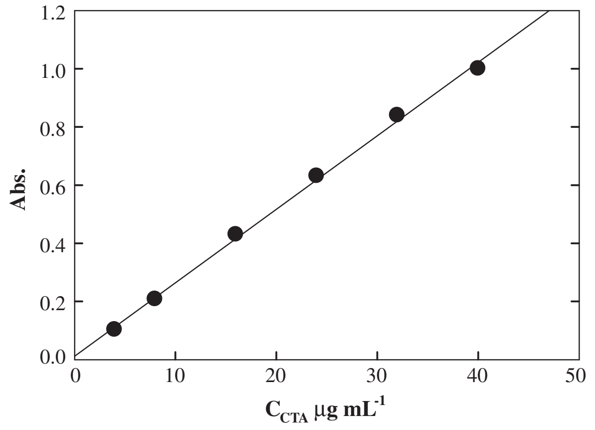


Figure 4 Beer's plot of CTA with TEA.

The limit of detection (LOD) and limits of quantification (LOQ) were also determined according to the IUPAC definitions by using the following formula:

$$\text{LOD or LOQ} = k\alpha/b \qquad (2)$$

where $k = 3$ for LOD and 10 for LOQ, α: is the standard deviation of the intercept, b: is the slope of the standard curve and k is the constant related to the confidence interval (IUPAC, 1981).

The (LOD), (LOQ), confidence intervals of slope and intercept and molar absorptivity values are compiled in Table 4. They recorded small values confirming the high sensitivity of the method. The high calculated molar absorptivity values indicate that the formed PT-complexes between CTA and the amines are highly stable.

3.5.2. Accuracy and precision of the method

The accuracy of the method was established by carrying out the analysis of solutions containing ten different concentrations of CTA within Beer's law limits followed by calculating the relative standard deviation and percentage recovery values. The absorbance of the PT-complex was measured at λ_{max} of the PT complex after mixing the selected concentrations as given in Table 4 with the optimum concentrations of the proton acceptors. The concentration is determined from the regression equation and the percentage recovery values were then calculated. The determined recovery values were found near 100% and the relative standard deviations (RDS) were less than 1%. This level of precision of the proposed method was adequate for the quality control analysis of CTA. The comparison between the mean and true value ($\overline{X} - \mu$) (Miller and Miller, 1988) with the largest difference that could be expected as a result of indeterminate error ($\pm tS/\sqrt{n}$) (Miller and Miller, 1988) was carried out and the results were compiled in Table 3. It has been found that ($\overline{X} - \mu$) were less than $\pm tS/\sqrt{n}$ indicating that no significant difference existed between the mean and the true values.

3.6. FTIR spectra

In order to identify the site of the interaction between CTA and amines, two solid complexes were isolated between CTA with BA and DMAN, respectively. The FTIR spectra of CTA and its complexes with BA and DMAN are shown in Fig. 5. Fig. 5a represents the FTIR spectrum of CTA where

Table 3 Quantitative parameters of the PT complexes.

Parameters	BA	TEA	PY	DMAN
Beer's law limits, μg mL^{-1}	4–40	4–40	4–40	4–40
Limit of detection, μg mL^{-1}	1.43	2.19	1.22	2.97
Limit of quantification, μg mL^{-1}	4.78	7.32	4.08	9.90
Molar absorptivity, L mol^{-1} cm^{-1}	10022	10107	12949	3827
Regression equation[*]				
Intercept, a	0.0133	0.0121	0.0149	0.1989
Slope, b	0.0250	0.0252	0.0324	0.0096
Confidence interval of intercept, α	±0.0213	±0.0330	±0.0236	±0.017
Confidence interval of slope, β	±0.0009	±0.0013	±0.0010	±0.0007
Correlation coefficient, R^2	0.9991	0.9978	0.9993	0.9960

[*] $Y = a + b X$ where Y is the absorbance for concentration, X in μg mL^{-1}.

Table 4 Accuracy and precision of the method.

Amine	Amount taken, μg mL^{-1}	Amount found, μg mL^{-1}	Average of Rec. (%)	S.E.	RSD, % ($n = 10$)	Average of $\lvert \overline{X} - \mu \rvert$	$\pm tS/\sqrt{n}$
BA	12.008	12.228	100.500	0.388	1.221	0.305	±0.925
	18.013	18.268					
	20.014	20.348					
	22.015	22.188					
	26.018	25.788					
	28.020	27.748					
	30.021	30.428					
	34.024	33.828					
	36.025	35.628					
	38.027	38.588					
TEA	12.008	12.099	101.499	0.400	1.246	0.375	±0.954
	18.013	18.171					
	20.014	20.750					
	22.015	22.218					
	26.018	27.020					
	28.020	28.528					
	30.021	30.234					
	34.024	34.520					
	36.025	36.187					
	38.027	38.210					
PY	12.008	12.318	99.158	0.471	1.501	0.357	±1.122
	18.013	17.873					
	20.014	19.664					
	22.015	21.855					
	26.018	25.620					
	28.020	27.256					
	30.021	29.910					
	34.024	33.552					
	36.025	35.281					
	38.027	38.151					
DMAN	12.008	11.885	100.172	0.300	0.948	0.188	±0.716
	18.013	17.927					
	20.014	20.323					
	22.015	21.885					
	26.018	26.469					
	28.020	27.927					
	30.021	30.115					
	34.024	34.073					
	36.025	36.365					
	38.027	37.823					

a sharp band at 3415 cm^{-1} was recorded which could be attributed to the $\nu(OH)$ stretching vibration of the free OH of CTA. A spitted band at 3120, 2728 and 2184 cm^{-1} was observed and attributed to $\nu(OHO)$ hydrogen bond of CTA.

Fig. 5b represents the FTIR spectrum of the complex (CTA–BA) where a sharp band at 3461 cm^{-1} was recognized and attributed to the free OH stretching vibration. A weak band at 3071 cm^{-1} was observed which could be assigned to $\nu(N^{+}H_3)$ and confirms the migration of the hydrogen bonded proton of CTA towards BA amino group, Scheme 3. Fig. 5c represents the FTIR spectrum of (CTA–DMAN) complex where a sharp band at 3423 cm^{-1} was observed corresponding to free OH stretching vibration.

Two Bohlman bands (Brzezinski et al., 1994) at 2337 and 2220 cm^{-1} representing the stretching vibrations of the two methyl groups, trans to the two lone pair of electrons of DMAN were recorded, confirming the migration of the hydrogen bonded proton towards the DMAN nitrogen centers, Scheme 3. Two bands at 845 and 778 cm^{-1} were also recorded and attributed to the stretching vibration of the symmetrical hydrogen bond (NHN), Scheme 3. Hence one can conclude from the FTIR spectral studies that the interaction site between CTA and amines is the hydrogen bonded hydroxylic group while the free OH group was the interaction site in solution.

4. Conclusion

The important conclusion that can be drawn from this work is the direct use of proton transfer reaction between chromotropic acid and some aliphatic and aromatic amines to develop a low cost, fast and accurate spectrophotometric method for the determination of chromotropic acid in the concentration range 4–40 μg mL^{-1}. This method was based on the simultaneous production of proton transfer complexes in a 1:1 ratio between CTA and some aliphatic and aromatic amines in methanol at 362 nm. Moreover the FTIR results confirmed that the interac-

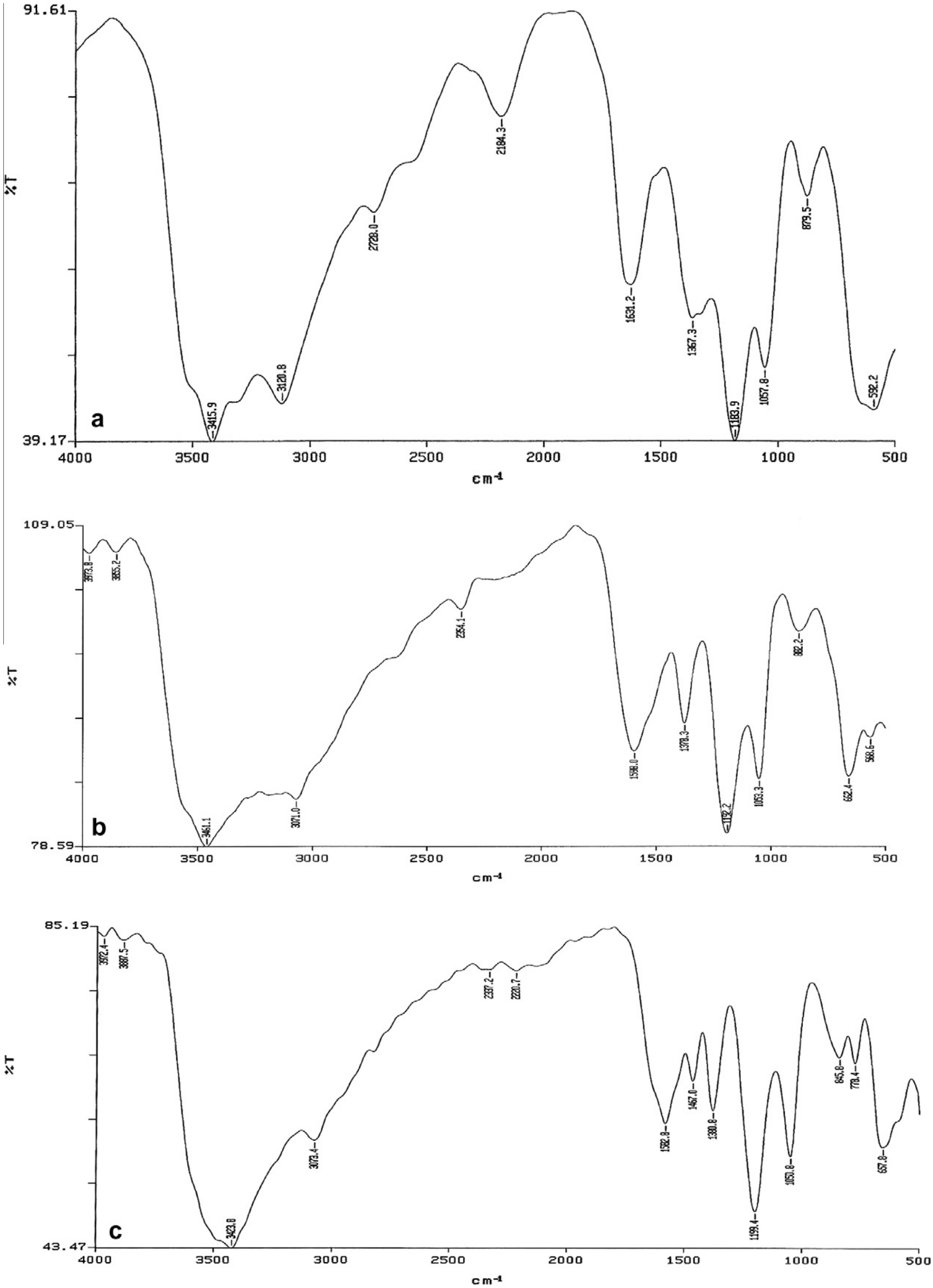
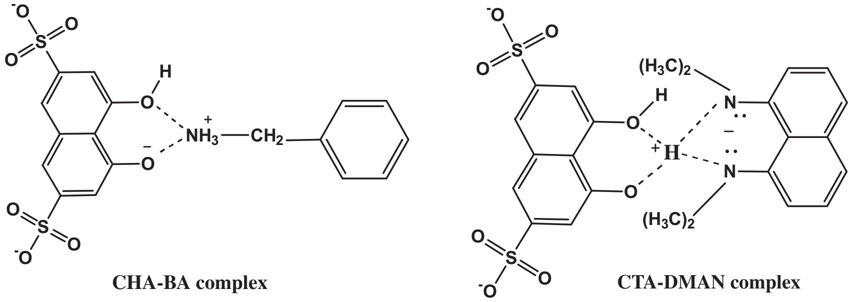


Figure 5 FTIR spectra of CTA (a) and its PT complexes with (b) BA and (c) DMAN in the range 4000–500 cm^{-1}.



CHA-BA complex CTA-DMAN complex

Scheme 3 Structures of (CTA–BA) and (CTA–DMAN) in the crystalline forms.

tion site in solution is the free OH group while the hydrogen bonded one is the site in the solid complexes.

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