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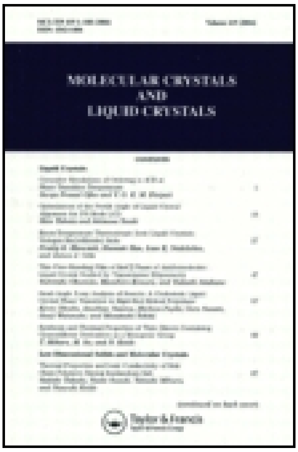

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FTIR Spectra of Hydrogen-Bonded Inclusion Compounds of Iodine

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FTIR Spectra of Hydrogen-Bonded Inclusion Compounds of Iodine

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The inclusion compounds of iodine such as α-cyclodextrin-KI-I_2-4H_2O, β-cyclodextrin-KI-I_2-H_2O, and amylose-iodine are hydrogen bonded with dyes such as Para red, Congo red, Direct red, Bismark brown, Trypan blue, and Evans blue. Hydrogen bonding of these with dyes containing O–H and N–H occurs in glucosidic oxygen atoms or O–H groups of the polysaccharides. Excitons are emitted and absorbed by the electrons along the iodine chains as revealed by the analysis, which reduces band gap along the polyiodide chains.

Keywords Exciton–phonon coupling; inclusion compounds; iodine chains; Little's model; Mott–Wannier excitons

Introduction

The inclusion compounds of iodine, also known as organic polyiodide chain complexes, have been studied in detail [1]. The structural, electrical, and optical properties of these complexes had been a subject of interest some time ago [2–6]. Pressure-induced Peierls instability has been proposed [7–9]. Six or seven sugar molecules form a cup- or cap-shaped molecules connected by glucosidic oxygen atoms. In the present work, many dyes are found to form hydrogen bonding at the site of glucosidic oxygen atoms or at the external O–H groups of these polysaccharides. Mott–Wannier excitons along the dyes resonate with electrons along the iodine chains. Excitons are emitted and absorbed, as required in Little's model for high-temperature superconductivity. It was proposed that if O–H groups of α- or β-cyclodextrins and amylose are replaced by dye molecules, the iodine chain may become superconducting [10–12]. We have tried here hydrogen bonding of oxygen atoms or O–H groups with dyes containing O–H and N–H groups.

Experimental

α-Cyclodextrin, β-cyclodextrin, and amylose in analytical reagent grade were obtained from Sigma Chemical Company. The inclusion compounds of K1–I_2 were precipitated by the evaporation method from aqueous solution. The blue-colored inclusion compounds were mixed with pure dyes such as Congo red, Direct red, Para red, Bismark brown,

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Trypan blue, and Evans blue, and ground till the color deepened. Grinding in an agate mortar with agate pestle led to molecular contact between the inclusion compounds and dye molecules.

The spectra in the range 400–4000 cm^{-1} were recorded using a GXFITR single-beam spectrophotometer (Perkin-Elmer Co., USA) having a resolution of 0.15 cm^{-1}, a scan range of 15600–30 cm^{-1} and a scan time of 20 sec. An optical path difference (OPD) velocity of 0.20 cm^{-1} and mid-infrared triglycine sulfate (MIRTGS) and far infrared triglycine sulfate (FIRTGS) detectors. A beam splitter of the opt KBr type was used, having a range of 7800–370 cm^{-1}. The spectra were recorded in purge mode.

Results and Discussion

The molecular structure of α-cyclodextrin along with hydrogen-bonded dyes (R) in oxygen atoms is shown in Fig. 1. The dyes provide highly polarizable side chains as required in Little's model. High polarizability of dye molecules means easy generation of electronic excitations (excitons) which are weakly bounded. It was realized that the band gap along the iodine chains was around 0.225 eV and β-cyclodextrin [13]. The band gap of dyes is also about the same order of magnitude as revealed by the infrared spectra of only dyes (see Figs. 2 and 3). Thus an interband transition along the iodine chain and along the dye molecules occurs at almost the same energy. The electronic excitation along dye molecules can be referred to generation of Mott–Wannier excitons.

The FITR spectra of α-cyclodextrin-KI-I_2-Para red, α-cyclodextrin-KI-I_2-Congo red, α-cyclodextrin-KI-I_2-Direct red, α-cyclodextrin-KI-I_2-Bismark brown, and α-cyclodextrin-KI-I_2-Evans blue are shown in Figs. 4 and 5. The interband transition (a transition from valance band to conduction band) is analyzed (see Figs. 6 and 7). In all cases, a break in the slope of a straight line in $\alpha h\nu$ versus $h\nu$ or $(\alpha h\nu)^{1/2}$ versus $h\nu$ or $(\alpha h\nu)^{1/3}$ versus $h\nu$ is observed in such a manner that the higher absorption has an intercept lower than the lower absorption cutting $h\nu$ axis at higher energy. This is in contrast

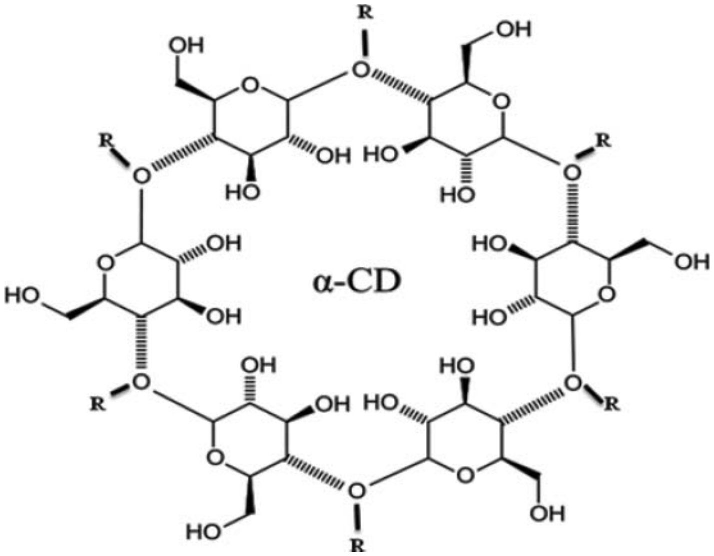


Figure 1. Molecular structure of α-cyclodextrin with hydrogen-bonded dyes (R).

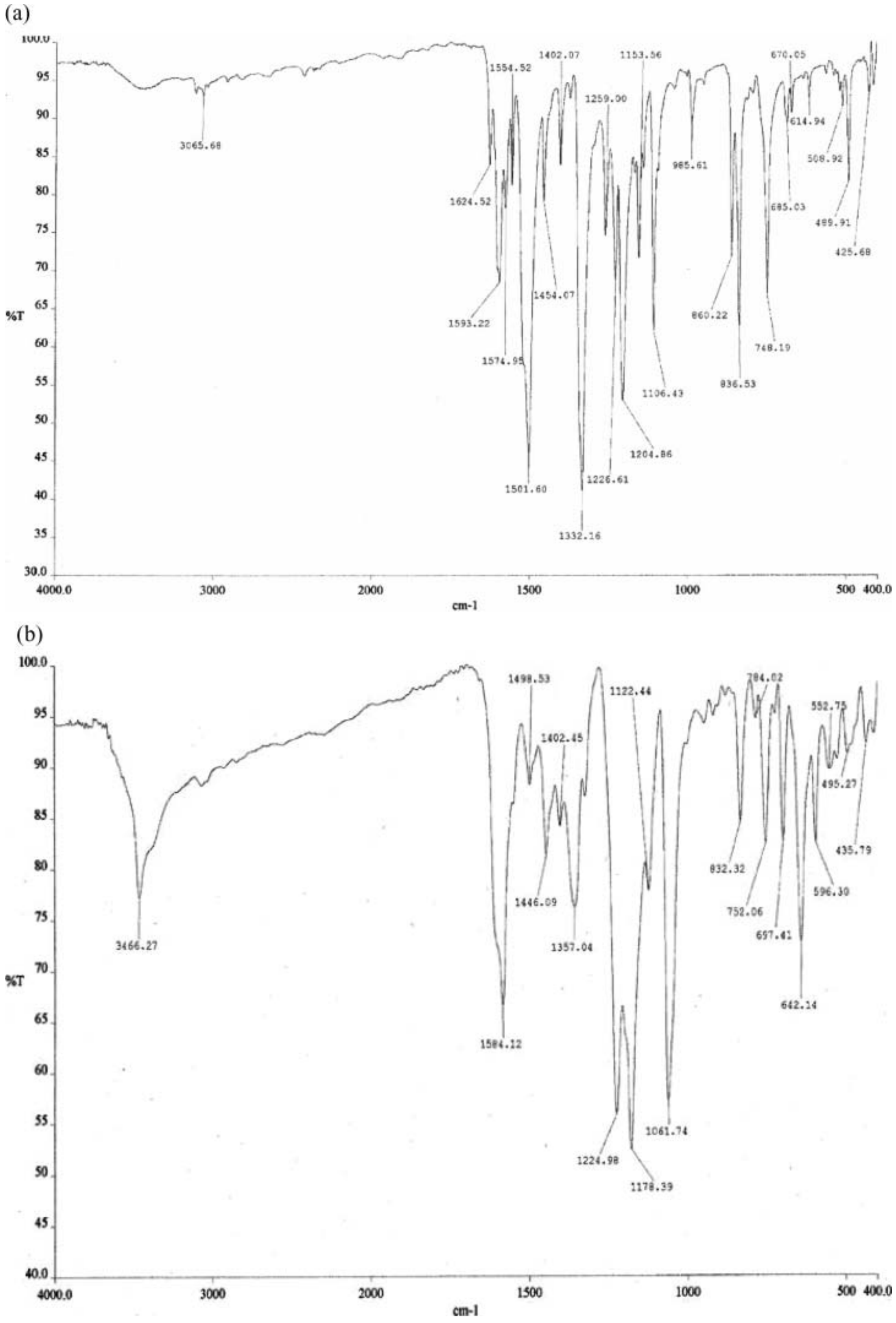


Figure 2. FTIR spectra of (a) Para red, (b) Congo red, and (c) Direct red.

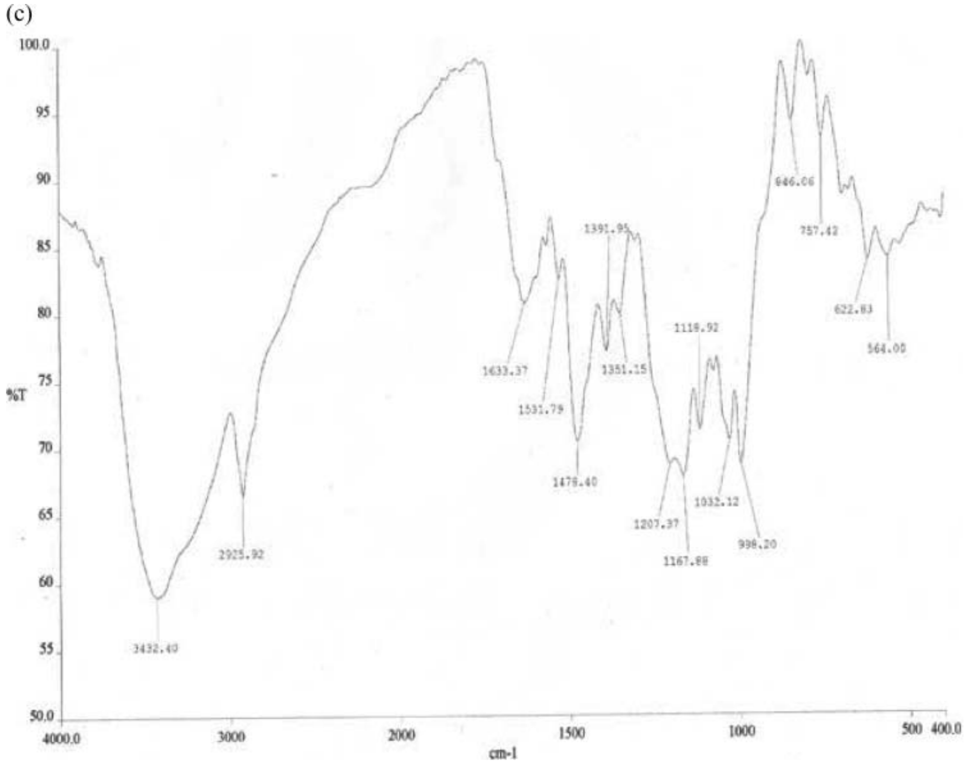


Figure 2. (Continued)

with indirect transition with phonon energy in which higher absorption has higher threshold than lower absorption having lower threshold. This inverted behavior is also found in some charge transfer complexes such as Ni(N-H-Salim)$_2$-DDQ, Ni(N-H-Salim)$_2$-TNF [14], Ni(N-C_2H_5-Salim)$_2$-TCNE [15], Ni(Hdpg)$_2$-TCNE [16], (DPPD)$_5$I$_{12}$ [17], and Cu(N-R-Salim)$_2$-PANI [18], where Salim = salicylaldiminato; Hdpg = diphenylglyoxime; DPPD = diphenyl p-phenylenediamine; R=H, CH_3, C_2H_5, and C_6H_5; and PANI = emeraldine, nigraniline, and pernigraniline. In the last case, emeraldine, nigraniline, and pernigraniline form hydrogen bonds with Cu(N-R-Salim)$_2$. We assign the inverted behavior of straight lines to the emission and absorption of excitons. The emission of excitons has lower threshold than the absorption of excitons. This inversion is intrinsically connected to the fact that phonon bands diminish at lower temperature, while exciton bands increase in intensity at low temperatures [19]. The emission threshold is lower than absorption threshold which also shows that first emission of excitons occurs and then absorption of excitons occurs which is logical. An electron along the iodine chain first excites a Mott–Wannier exciton (an excitation across the band gap along iodine chain) of dye molecule and other electron absorbs the exciton. Thus emission of an exciton is a primary process and absorption of an exciton is a consequent secondary process. There is excitonic reduction in the band gap along iodine chains. In α-cyclodextrin-KI-I_2-4H_2O, there is an allowed direct transition with $(\alpha h\nu)^{1/2}$ versus $h\nu$ being a straight line. Here $(\alpha h\nu)$ versus $h\nu$ as in two-dimensional conductor or $(\alpha h\nu)^{1/2}$ versus $h\nu$ or $(\alpha h\nu)^{1/3}$ versus $h\nu$ plots shows straight lines revealing

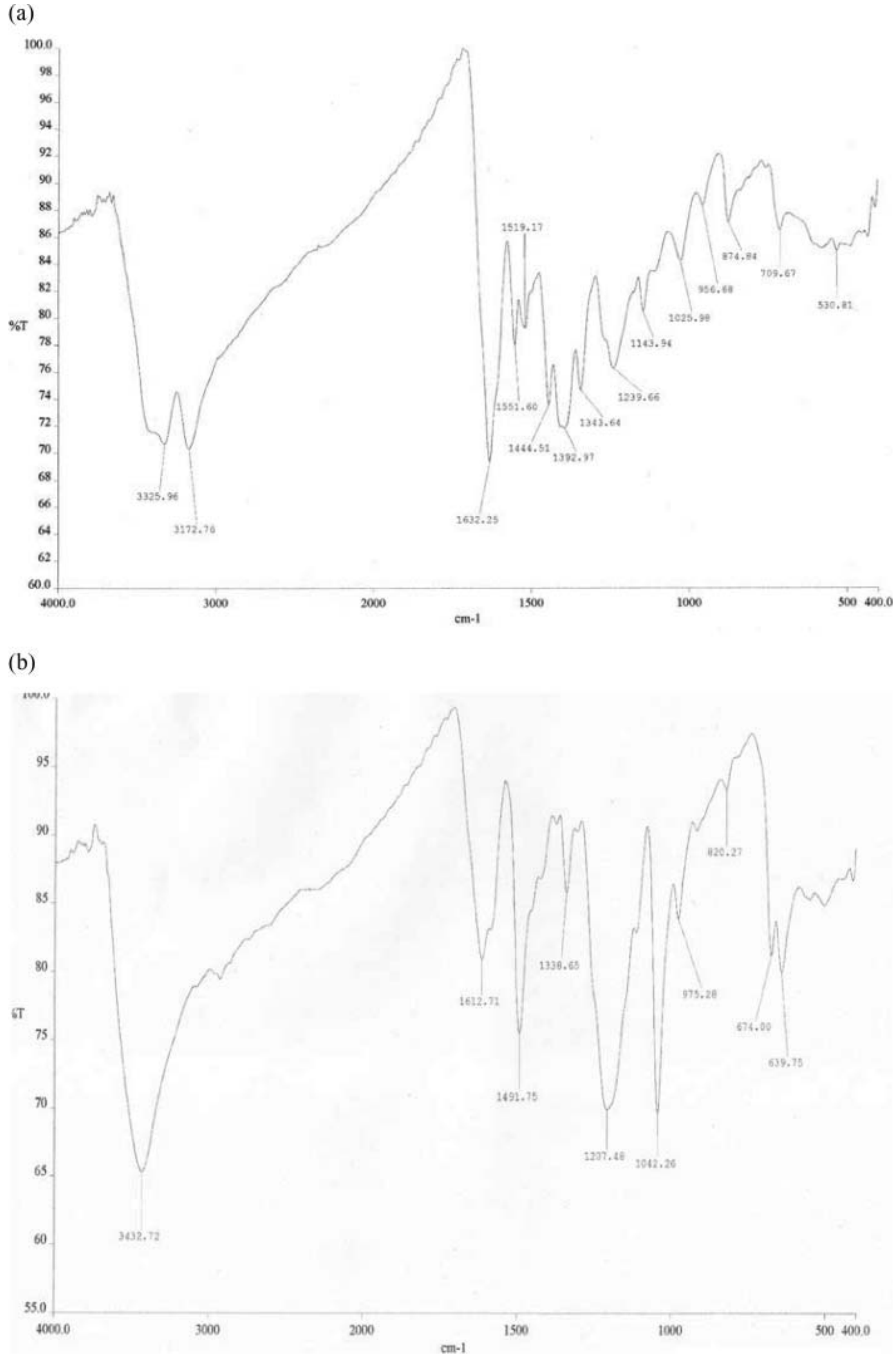


Figure 3. FTIR spectra of (a) Bismark brown, (b) Trypan blue, and (c) Evans blue.

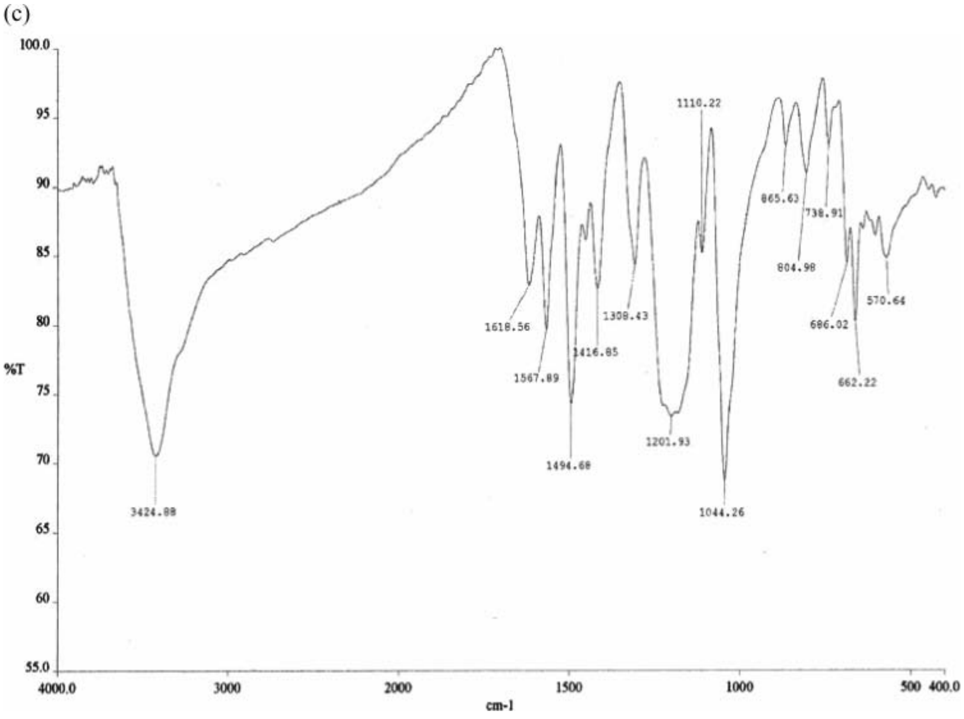


Figure 3. (Continued)

the allowed indirect transition or forbidden indirect transition in one-dimensional semiconductor. Thus electron–phonon interaction along the iodine chains also occurs, leading to an indirect transition. This is probably due to the exciton–phonon interaction [19]. Excitons are also able to excite phonons, leading to an indirect transition. The exciton–phonon coupling can also be explained with polaronic excitons in which electronic polaron and hole polaron form bound pairs. It is one type of bipolaron.

The results can also be explained with heavy doping of dye, i.e., an excitonic medium. The Burstein–Moss shift (ξ_n or ξ_p) can lead to an increase in band gap which is not observed. Rather there is an additional shrinkage (Δ_0 or Δ_1) of the gap due to heavy doping of excitonic medium; Δ_0 is the additional shrinkage for the direct transition and Δ_1 is the additional shrinkage for the indirect transition [20–22]. In this case, the difference in intercept can be expressed in meV and can be explained with Δ_0 or Δ_1.

The electron–electron scattering is a momentum conserving mechanism and an exciton is exchanged between two electrons along the iodine chains. The additional shrinkage of the gap is due to the electron–electron indirect interaction. There is also an increased absorption or optical conductivity arising from a conductive (an inverse of resistive transition) transition and exciton–phonon coupling apart from excitonic interaction. This decreases activation energy. The exciton–phonon coupling leads to bumps in absorption or optical conductivity [22].

The spectra of β-cyclodextrin-KI-I_2-Para red, β-cyclodextrin-KI-I_2-Direct red, β-cyclodextrin-KI-I_2-Bismark brown, β-cyclodextrin-KI-I_2-Trypan blue, and β-cyclodextrin-KI-I_2-Evans blue are also shown (see Figs. 8 and 9). The interband transitions are analyzed

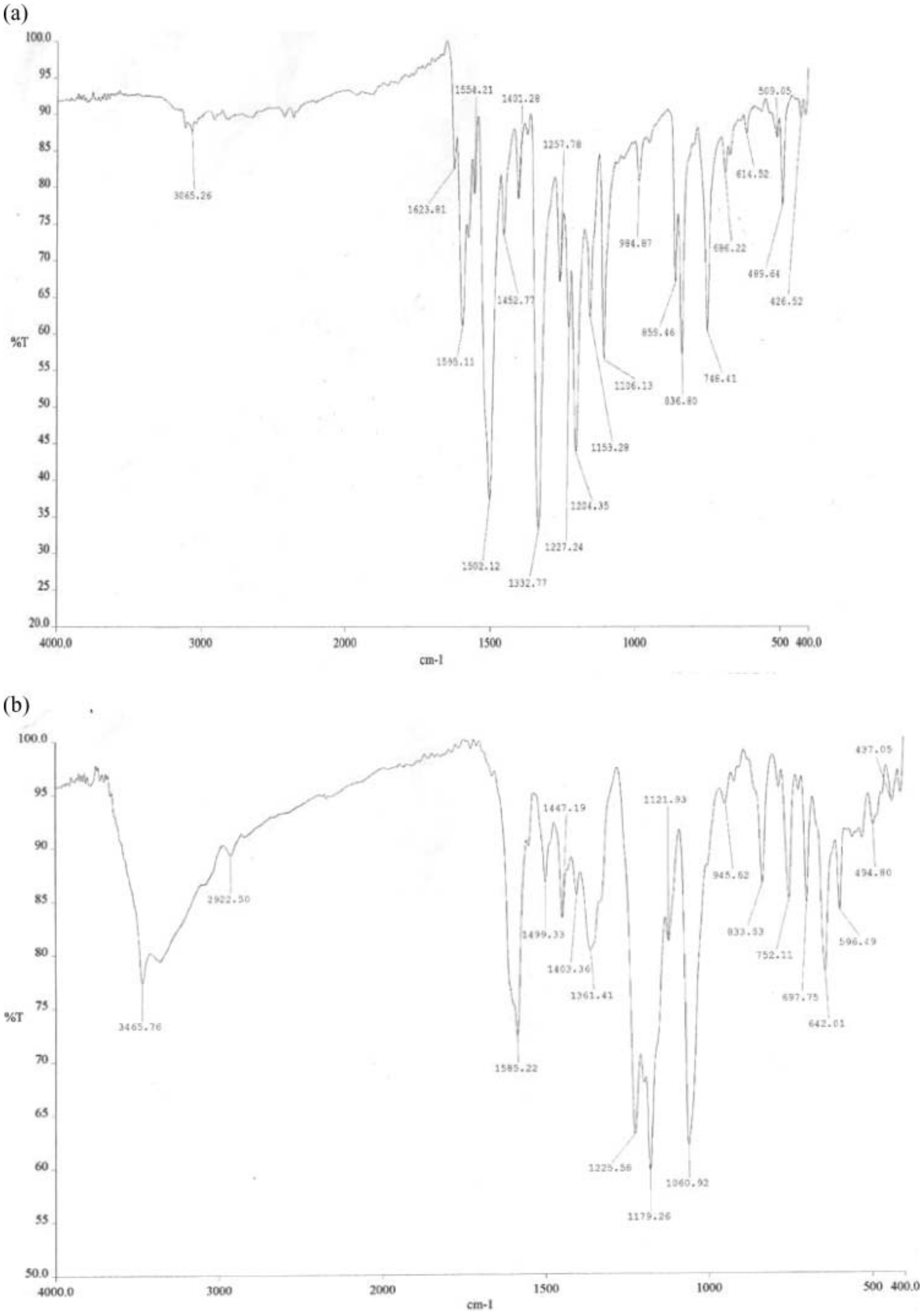


Figure 4. FTIR spectra of (a) α-cyclodextrin-KI-I_2-Para red, (b) α-cyclodextrin-KI-I_2-Congo red, and (c) α-cyclodextrin-KI-I_2-Direct red.

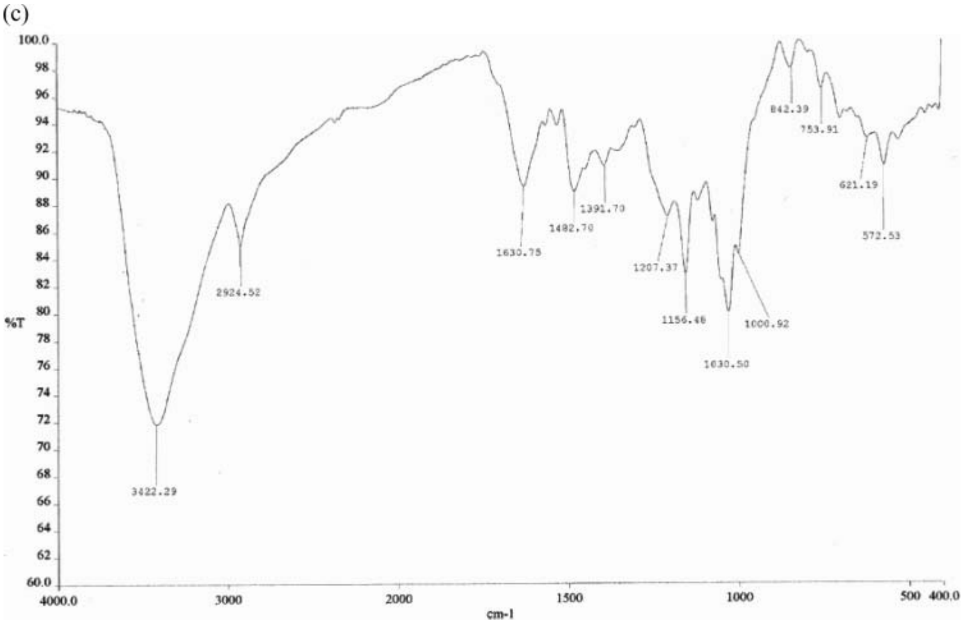


Figure 4. (Continued)

Table 1. Band gaps and exciton energy (E_{exc}) for various inclusion compounds of iodine hydrogen bonded with dyes

Name of the complex	Band gap E_g (eV)	Exciton energy E_{exc} (meV)
α-Cyclodextrin-KI-I_2-Bismark brown	0.218	21.6
α-Cyclodextrin-KI-I_2-Direct red	0.215	33.0
α-Cyclodextrin-KI-I_2-Evans blue	0.220	31.6
α-Cyclodextrin-KI-I_2-Para red	0.208	73.0
α-Cyclodextrin-KI-I_2-Congo red	0.156	41.2
α-Cyclodextrin-KI-I_2-Trypan blue	0.177	83.6
β-Cyclodextrin-KI-I_2-Bismark brown	0.213	40.6
β-Cyclodextrin-KI-I_2-Direct red	0.224	61.4
β-Cyclodextrin-KI-I_2-Evans blue	0.220	31.3
β-Cyclodextrin-KI-I_2-Para red	0.224	20.3
β-Cyclodextrin-KI-I_2-Trypan blue	0.238	59.8
Amylose-KI-I_2-Bismark brown	0.213	29.4
Amylose-KI-I_2-Congo red	0.180	48.4
Amylose-KI-I_2-Direct red	0.165	71.9
Amylose-KI-I_2-Para red	0.189	12.3

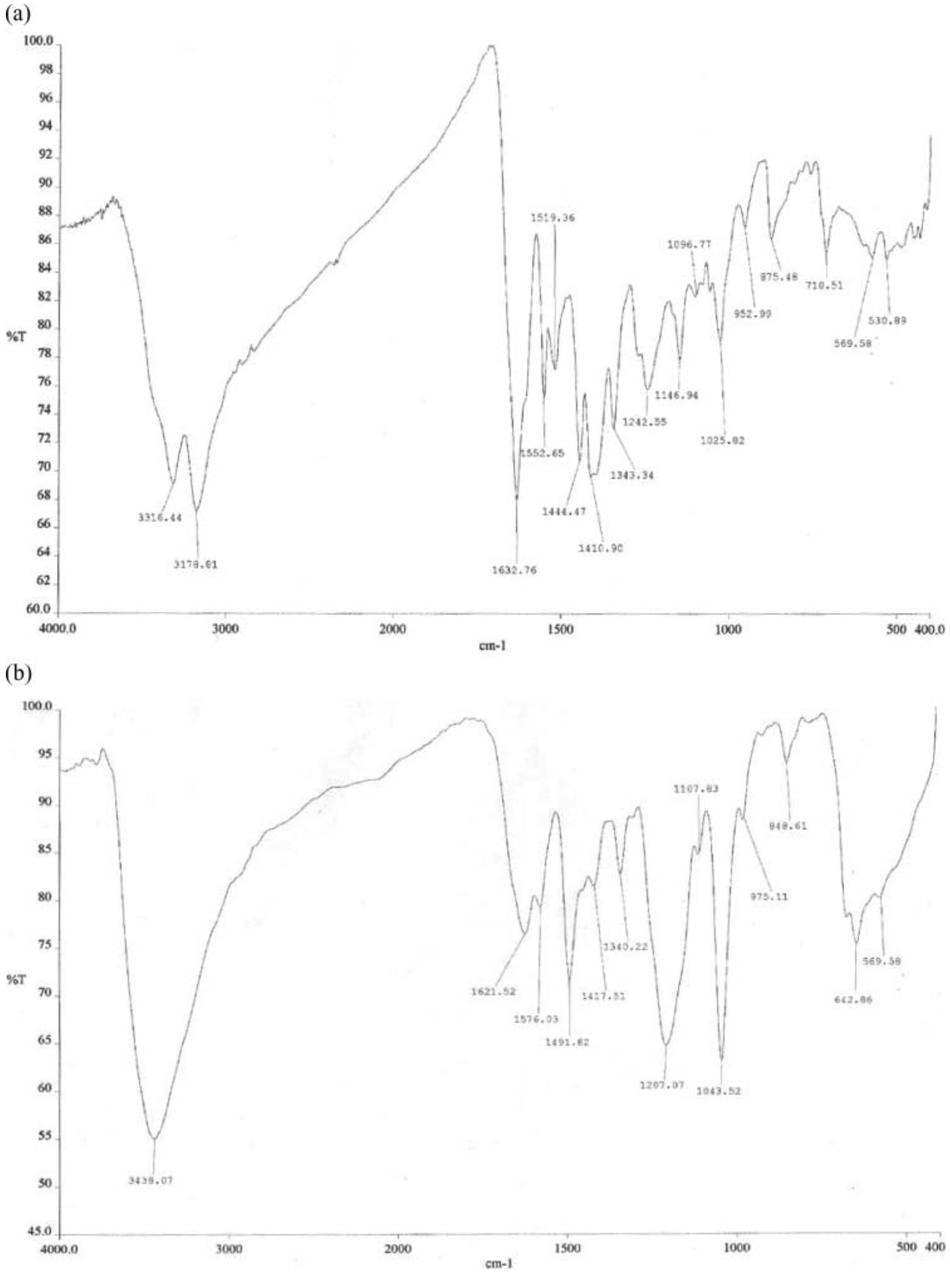


Figure 5. FTIR spectra of (a) α-cyclodextrin-KI-I_2-Bismark brown, (b) α- cyclodextrin-KI-I_2-Trypan blue, and (c) α-cyclodextrin-KI-I_2-Evans blue.

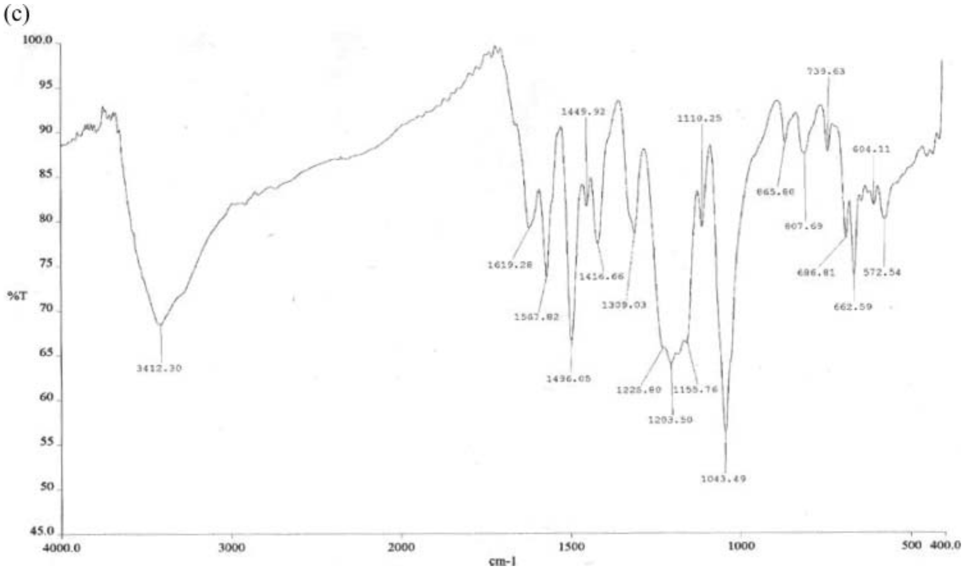


Figure 5. (Continued)

(see Figs. 10 and 11). Similarly the spectra of amylose-KI-I_2-Para red, amylose-KI-I_2-Congo red, amylase-KI-I_2-Direct red, and amylose-KI-I_2-Bismark brown are shown (see Figs. 12 and 13). The interband transitions are also analyzed (see Fig. 14). The results and analysis are similar to those of the hydrogen-bonded complexes of α-cyclodextrin-KI-I_2-$4H_2O$, and only in amylose-KI-I_2-Para red, a jump in absorption corresponding to a conductive transition is observed, which increases conductivity at higher energy. A total increase in conductivity of about two orders of magnitude is expected from such a conductive transition, exciton–phonon coupling, and additional shrinkage of the band gap.

There is also exciton–exciton coupling due to formation of excitons along the iodine chains. These exciton–exciton couplings are of two types. There can be resonant coupling due to the in-phase process of creation and annihilation of excitons or it can be antiresonant coupling due to the out-of-phase process of creation and annihilation of excitons.

In the present work, the absorption coefficients are found to follow: $Ah\nu = A(h\nu - E_g + E_{\text{exc}} \pm E_p)$ corresponding to the allowed indirect or direct transition in two dimensions; $\alpha h\nu = A(h\nu - E_g + E_{\text{exc}} \pm E_p)^2$ corresponding to the allowed indirect transition in one dimension; and $\alpha \text{h}\nu = A(h\nu - E_g + E_{\text{exc}} \pm E_p)^3$ corresponding to the forbidden indirect transition in one dimension. Here E_g is the band gap, E_{exc} is the exciton binding energy expressed in meV for the Mott–Wannier type exciton and E_p is the phonon energy. Band gaps and exciton energies are listed in Table 1.

Conclusion

The FTIR spectra of three inclusion compounds, namely, α-cyclodextrin-KI-I_2, β-cyclodextrin-KI-I_2, and amylose-KI-I_2 when further hydrogen bonded with various dyes, have been obtained and analyzed. The analysis of the interband transition reveals an indirect electron–electron interaction through the Mott–Wannier exciton across dye molecules.

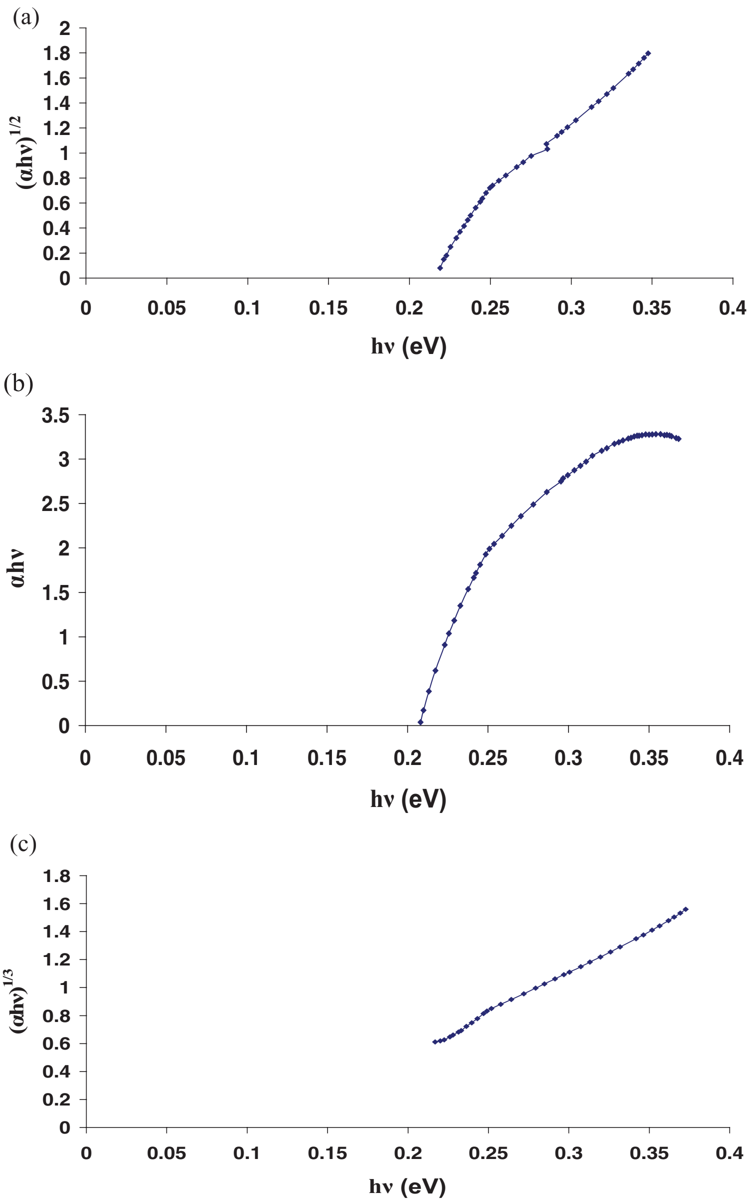


Figure 6. Analysis of the interband transition for (a) α-cyclodextrin-KI-I_2-Direct red, (b) α-cyclodextrin-KI-I_2-Para red, and (c) α-cyclodextrin-KI-I_2-Congo red.

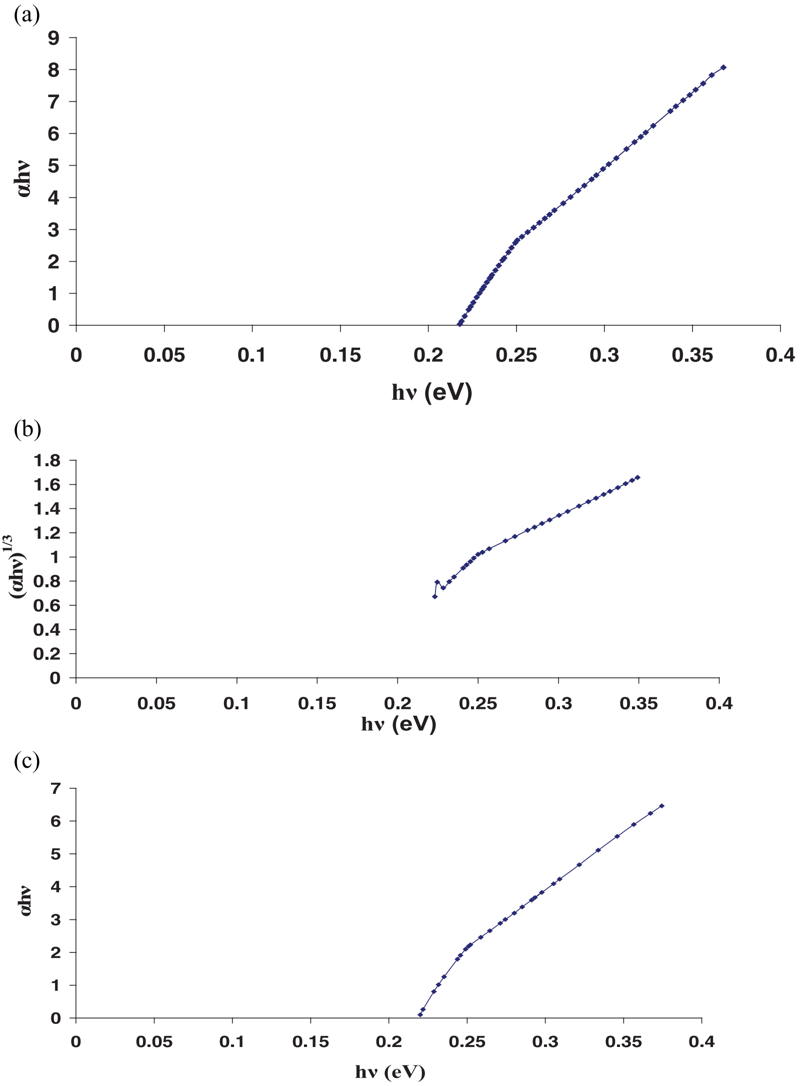


Figure 7. Analysis of the interband transition for (a) α-cyclodextrin-KI-I_2-Bismark brown, (b) α-cyclodextrin-KI-I_2-Trypan blue, and (c) α-cyclodextrin-KI-I_2-Evans blue.

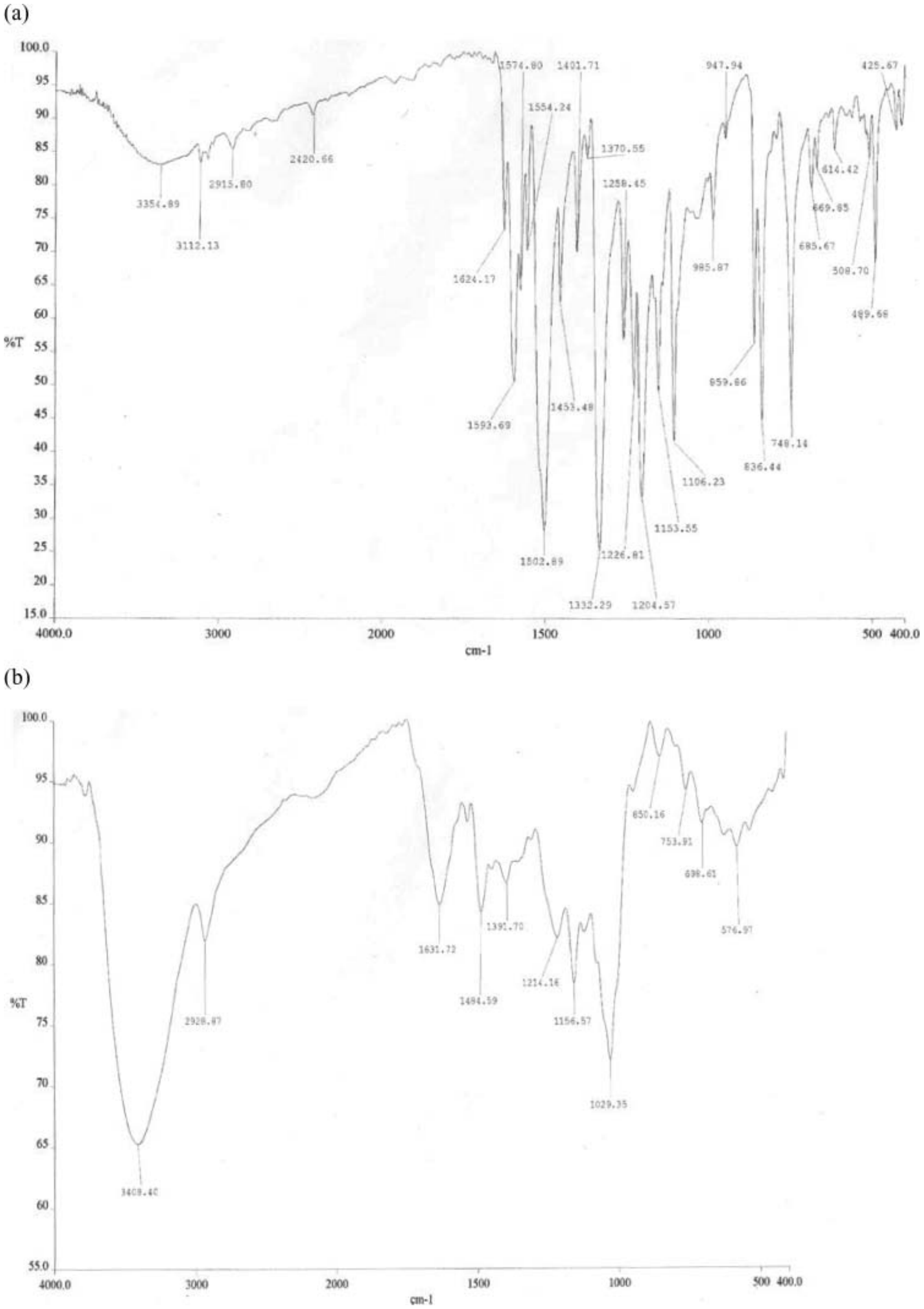


Figure 8. FTIR spectra of (a) β-cyclodextrin-KI-I$_2$-Para red and (b) β-cyclodextrin-KI-I$_2$-Direct red.

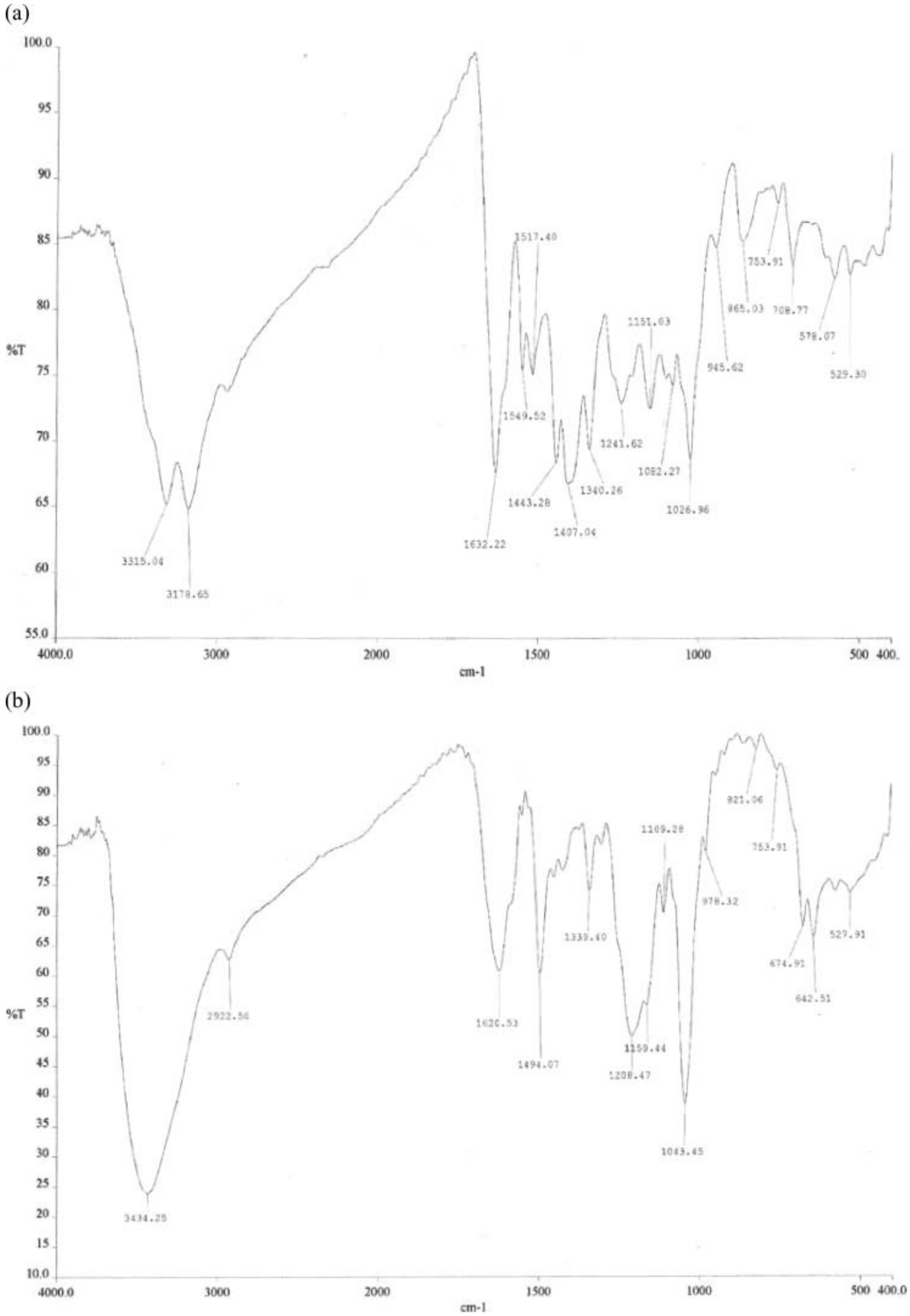
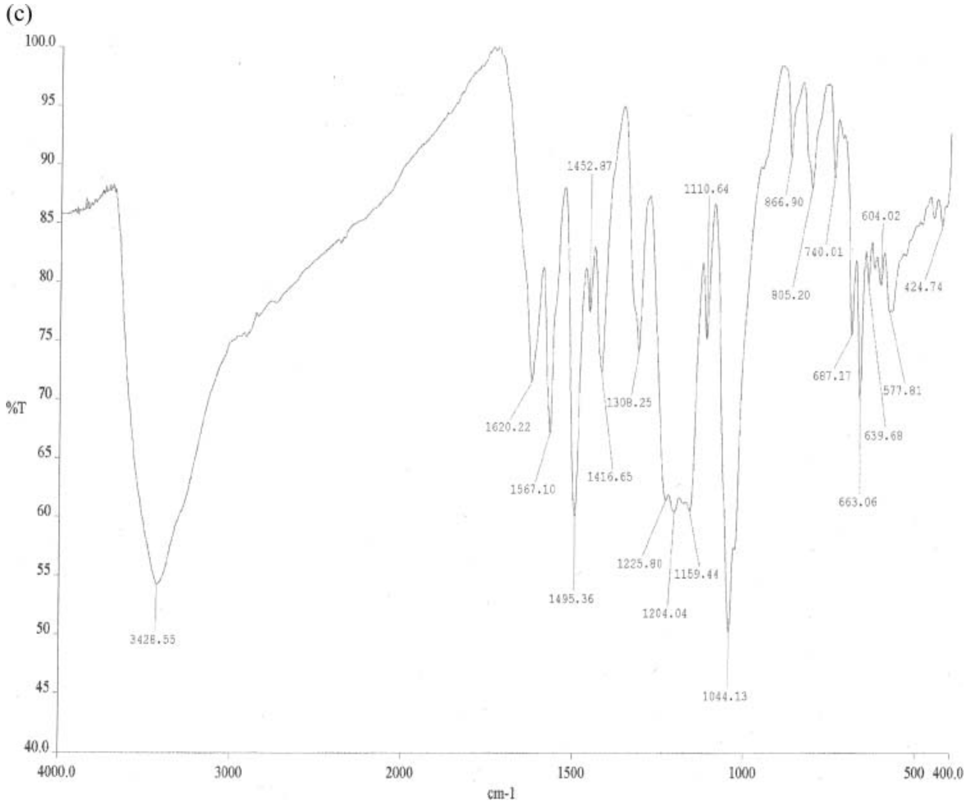


Figure 9. FTIR spectra of (a) β-cyclodextrin-KI-I_2-Bismark brown, (b) β-cyclodextrin-KI-I_2-Trypan blue, and (c) β-cyclodextrin-KI-I_2-Evans blue.



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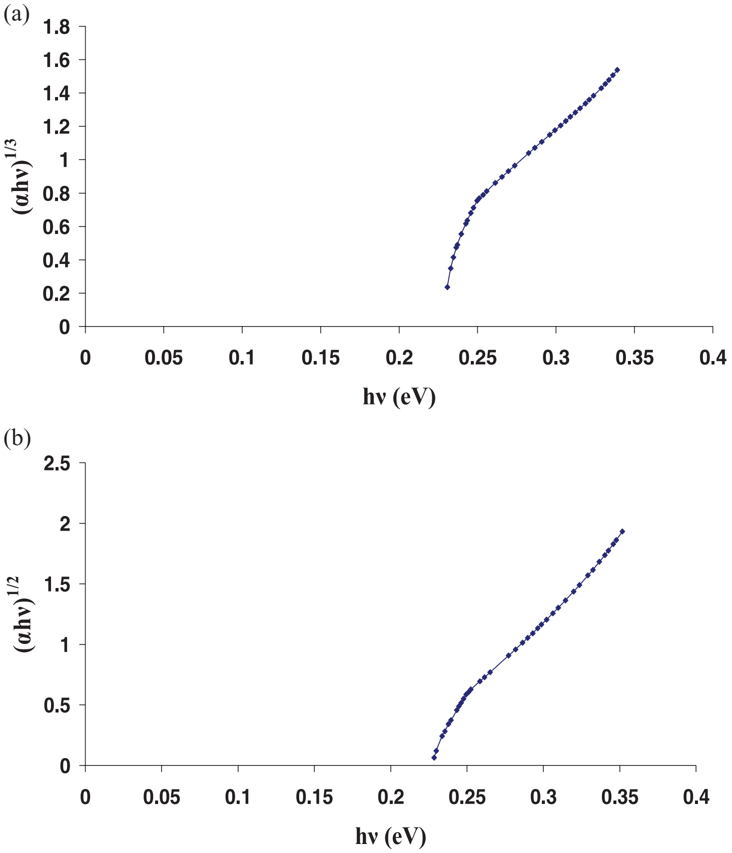

Figure 10. Analysis of the interband transition for (a) β-cyclodextrin-KI-I_2-Direct red and (b) β-cyclodextrin-KI-I_2-Para red.

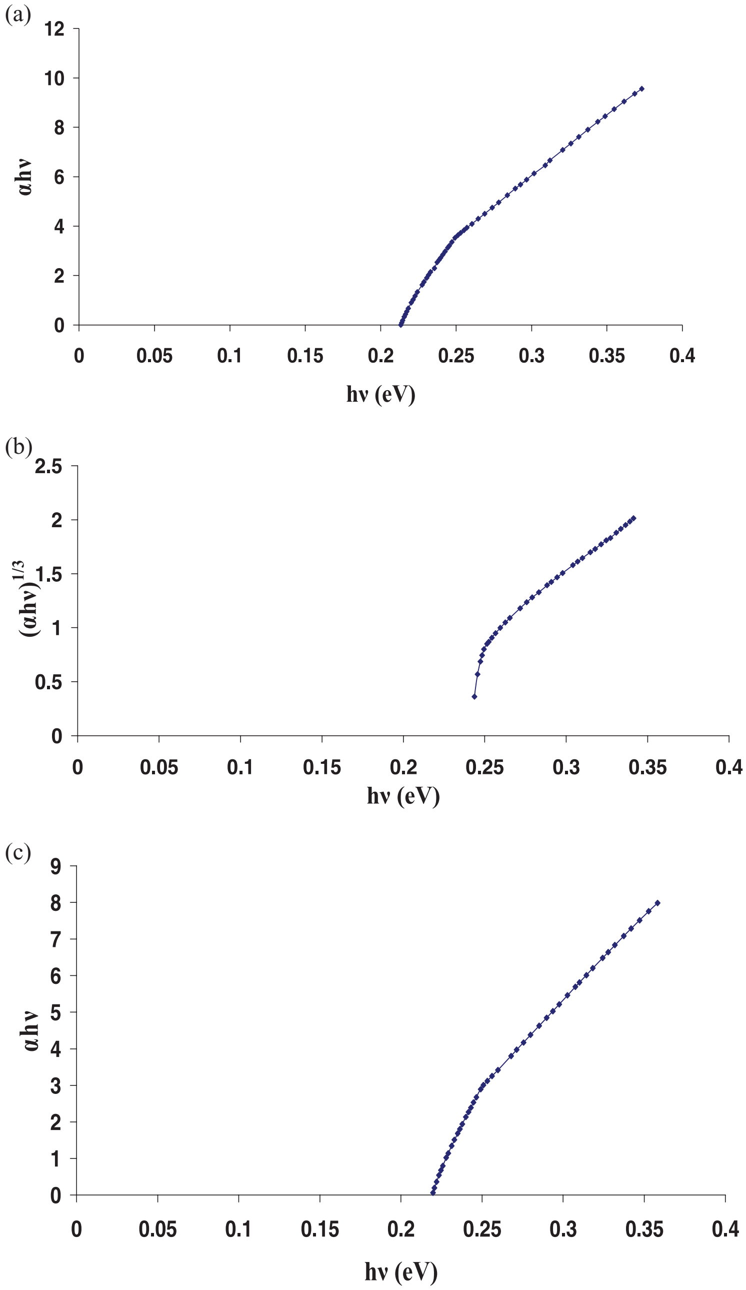

Figure 11. Analysis of the interband transition for (a) β-cyclodextrin-KI-I_2-Bismark brown, (b) β-cyclodextrin-KI-I_2-Trypan blue, and (c) β-cyclodextrin-KI-I_2-Evans blue.

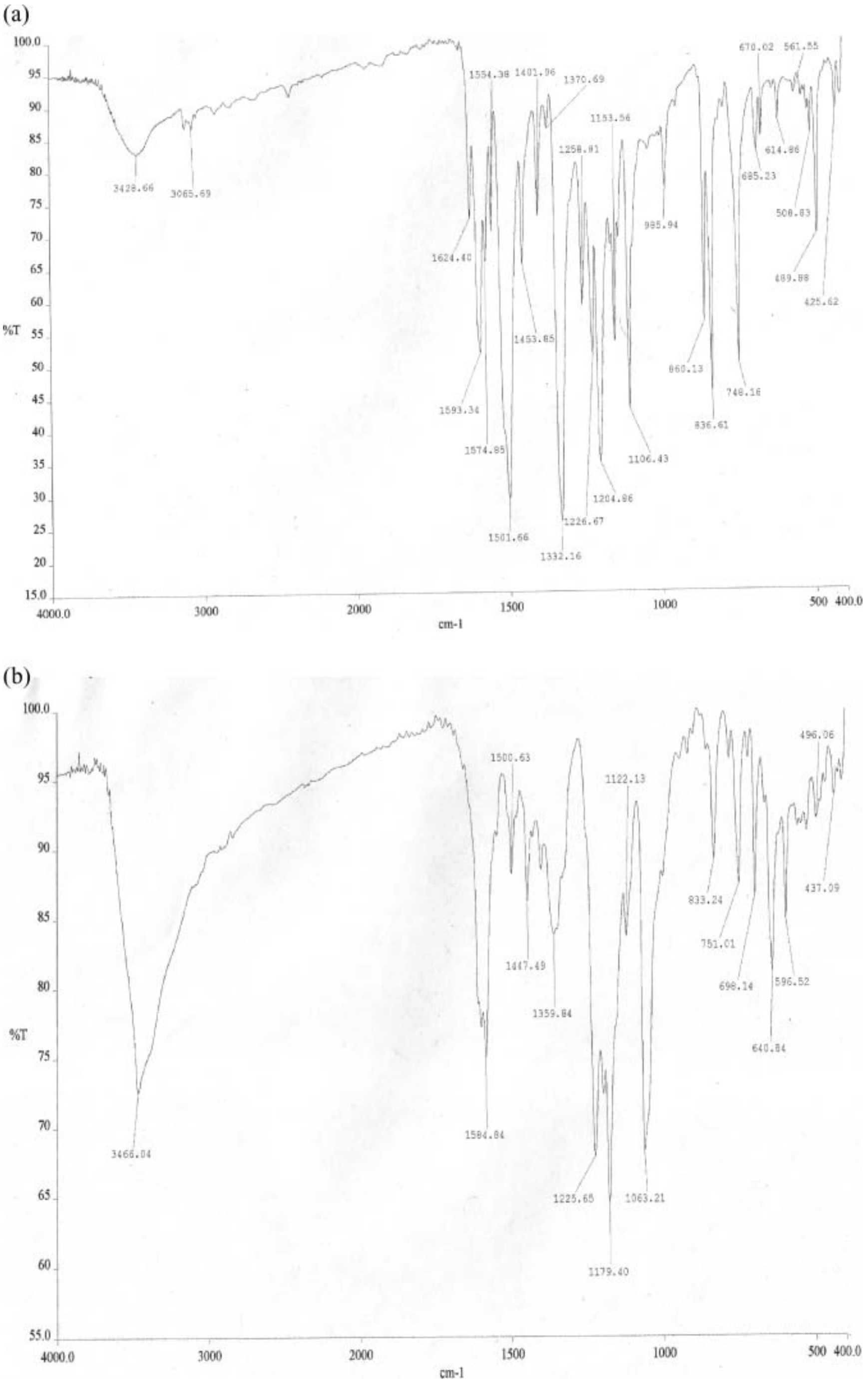

Figure 12. FTIR spectra of (a) amylose-KI-I_2-Para red and (b) amylose-KI-I_2-Congo red.

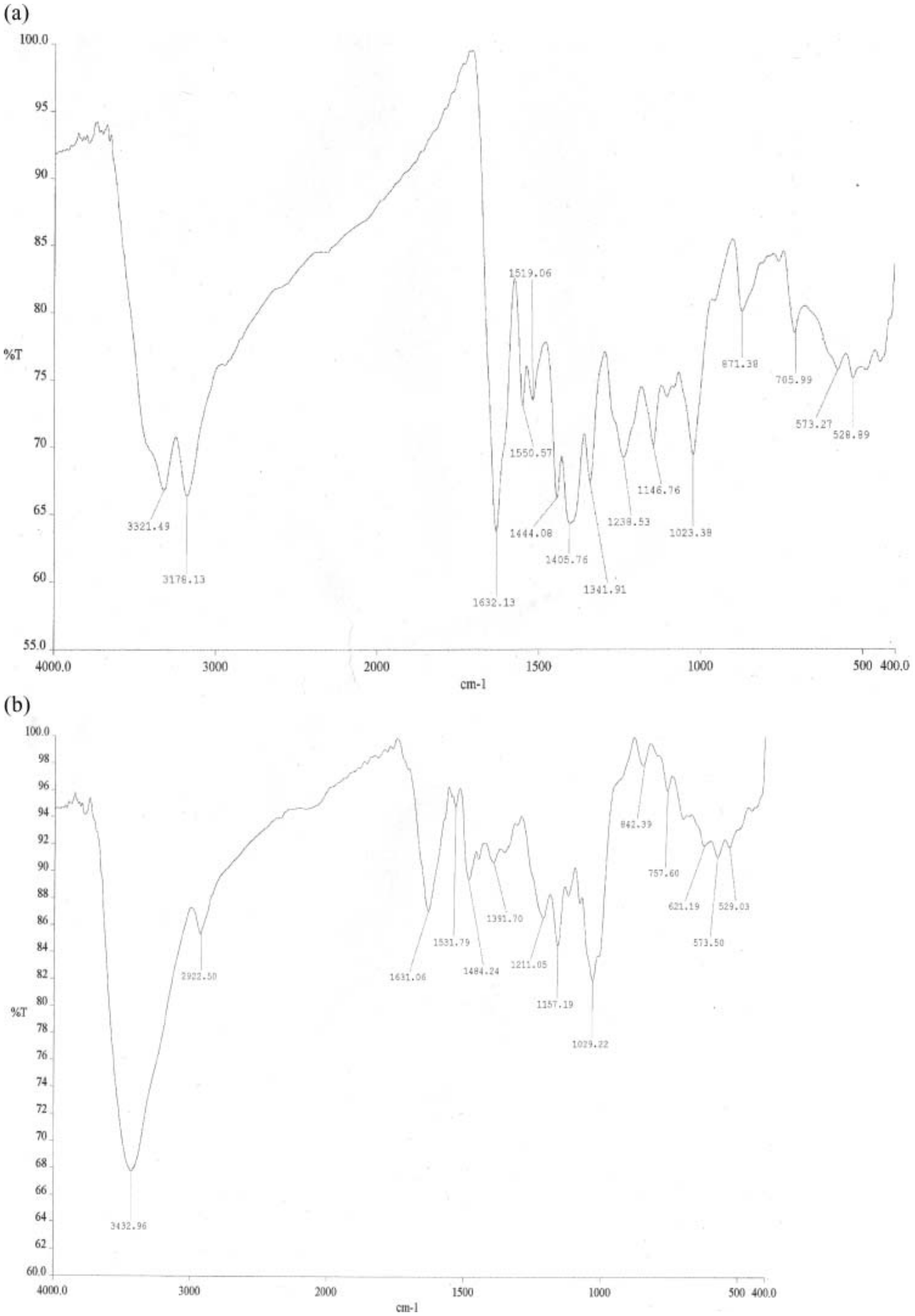

Figure 13. FTIR spectra of (a) amylose-KI-I_2-Bismark brown and (b) amylose-KI-I_2-Direct red.

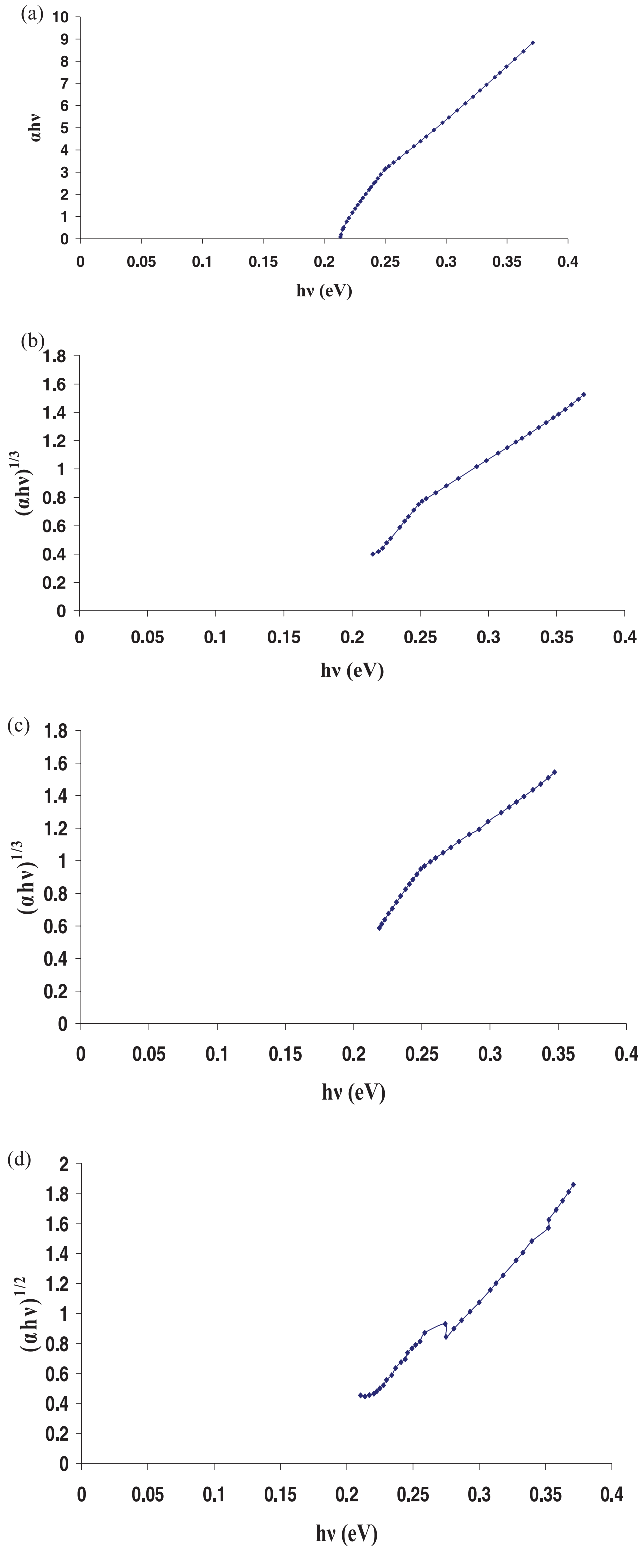

Figure 14. Analysis of the interband transition for (a) amylose-KI-I_2-Bismark brown, (b) amylose-KI-I_2-Congo red, (c) amylose-KI-I_2-Direct red, and (d) amylose-KI-I_2-Para red.

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