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*p*ISSN: 1220-871X *e*ISSN: 1844-0401

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FTIR AND MOLECULAR MODELING STUDY OF THE INTERACTION BETWEEN β-CYCLODEXTRIN AND POLYCHLOROBIPHENYLS

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abstract: The production of polychlorobiphenyls (**PCB**'s) is forbidden but they are found frequently in different environmental compartment due to their high stability. In this paper the interaction between β-cyclodextrin (**β-CD**), a chiral selector, and a mixture of PCB's, extracted from transformer oil, with 3 to 8 chlorine atoms was studied by FTIR spectrometry. The spectra of β-cyclodextrin in solid state obtained by KBr pellets technique and in saturated aqueous solutions obtained using CaF_2 windows ($1{,}5\cdot10^{-3}$ M), of PCB's mixture in $C_6H_3Cl_3$ solution and the spectra of different phases of ternary **PCB-$C_6H_3Cl_3$-H_2O** and quaternary **PCB-$C_6H_3Cl_3$-β-CD-H_2O** systems were examined. The interaction was evidenced after changes in intensity of C=C vibrations band with maximum positioned at 1647.90, 1645.90 cm^{-1} Limits of the study due to work conditions are discussed. Molecular modeling offered information on the stability of the complexes.

key words: PCB's; cyclodextrin; FTIR; interaction; molecular modeling.

received: December 2, 2010 *accepted*: December 23, 2010

1. Introduction

Although the use of polychlorobiphenyls was banned after 1980, the problems caused by these serious pollutants persist due to their stability and recurrence in all environment compartments.

Considering the big number of PCB congeners (209) these may be identified in the majority of circumstances with the help of two GC columns using stationary phase characterized by disparate separating powers with an electron capture or mass spectral detection [1]. But in the case of microbial, thermal or photolytic degradation the appearance of PCB's not normally found in environment, will require more stringent chemical structure determination, discrimination between isomers with the same number of chlorine atoms. The infrared spectra of PCB's congeners are surprisingly characteristic, even between highly chlorinated isomers [3]. Two infrared techniques have recently became available:

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trapping columns affluent on a liquid nitrogen cooled zinc/selenium disc, followed by Fourier Transform attenuated reflectance spectroscopy [4] and observing the column effluent in real time using a gold plated high pipe and optical bench in the vertical plane [5]. This last hyphenated technique has been further enhanced by the introduction of an array processor dedicated to the Fourier Transform, *i.e.* a device which greatly increases the speed of transform. Using the second technique Bush & Bernard [6] report the gas phase infrared spectra of all 209 possible PCB congeners and evaluate the technique for quantitative analysis of PCB's.

On the other hand cyclodextrins are reported in the recent years as stationary phase in GC-MS [7,8] in analysis of complex matrices containing PCBs. The cyclodextrins can effectively immobilize the toxic compounds as PCB's between its rings [9]. For this reason the host-guest type interaction between PCB and cyclodextrins was studied by FTIR spectroscopy in solution and molecular modelling.

2. Experimental Part

Beta-cyclodextrin p.a., Sigma Aldrich and a complex mixture pf PCB's with 3 to 8 chlorine atoms (extracted from transformer oil) as stock solution of PCB in $C_6H_3Cl_3$ ($1,5 \cdot 10^{-3}$ M) were used.

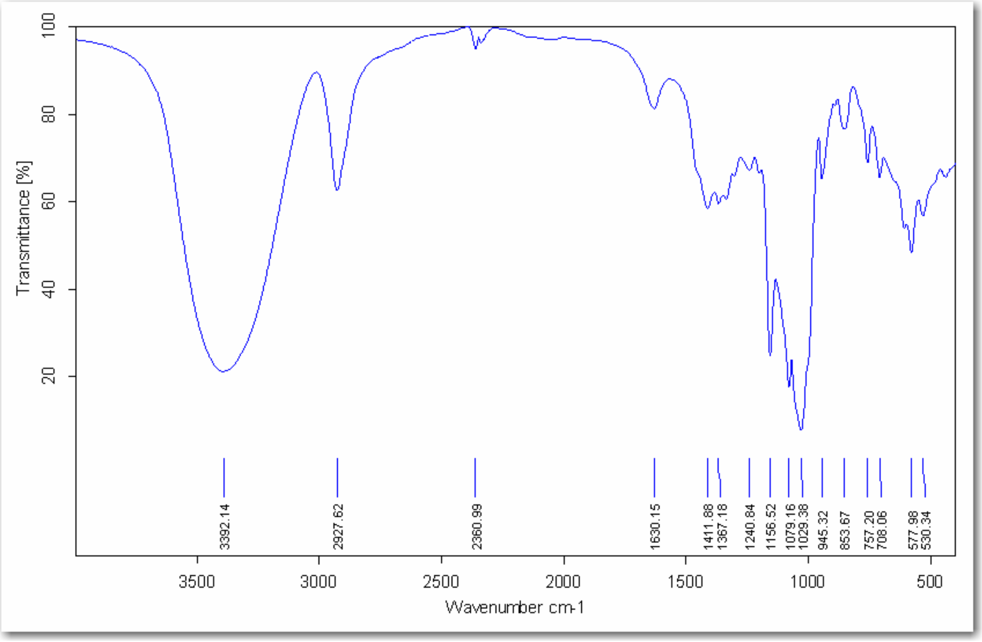


Fig. 1 *β-CD FTIR spectra obtained with the KBr pellet technique.*

For β-CD were carried out the FTIR spectra of pure powder by KBr pellets technique (Fig. 1) and of saturated aqueous solution (Fig. 2) using CaF_2 windows (these windows are transparent for infrared radiation up to 1200 cm^{-1} and resistant in aqueous medium). For

PCBs mixture (containing 60% PCB in C_6H_3Cl) were carried out the FTIR spectra of stock solutions (Fig. 3) and those corresponding to the different phases of the ternary system containing 1ml PCB and 2 ml saturated solution of β-CD (Fig. 4).

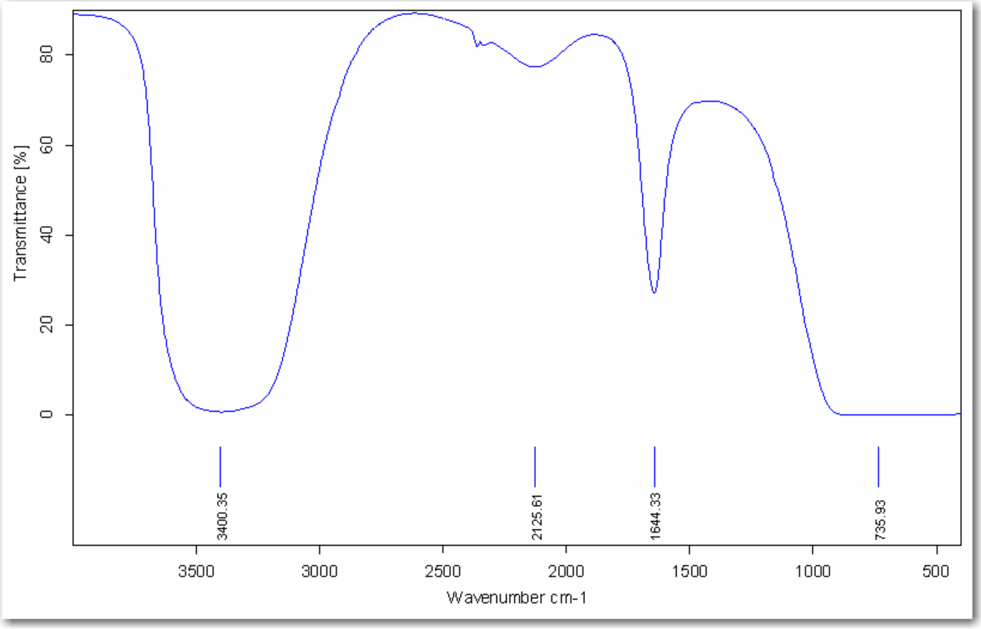


Fig. 2 β-*CD FTIR spectra in aqueous solution obtained using* CaF_2 *windows.*

IR spectra were carried out on a Bruker Vertex 70 FTIR spectrometer in the range 4000÷400 cm^{-1} with a 4 cm^{-1} resolution in transmission.

The formation of the complexes between PCB's (mono (2), di (2,2') and three (2,2',3) chloro) and beta- and gamma-cyclodextrins was studied by molecular modeling. The MM+ force field, implemented in the Hyperchem program was used. The Polack-Ribiere algorithm and the Root Mean Square gradient of 0.01 kcal/mol·Å were employed.

3. Results and discussion

Based on knowledge of the literature sources [6,9] and the use of modern IR spectrometers library [3] one may expect appearance and changes in position and intensity of the infrared absorption bands for the partners of interaction.

Analysing the spectra of β-CD (Figs. 1 and 2) of PCB's stock solution (Fig. 3) and of ternary system (Fig. 4) one may conclude that due to the large and strong band of γOH from β-CD in solution (Fig. 2) the domain of 3000 cm^{-1} corresponding to C-H stretching vibrations of PCB is not accessible to observation in the spectra of ternary system (Fig. 4). Because of limited transparency of CaF_2 windows the range of wavenumbers under 1000 cm^{-1} where are the C-Cl vibrations is not available (Figs. 3 and 4).

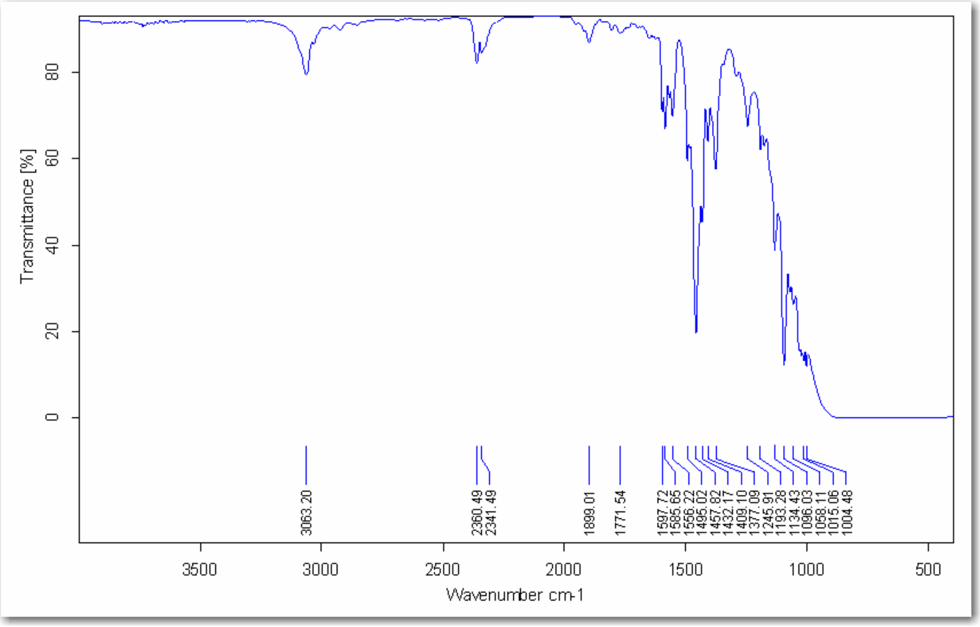


Fig. 3 *PCB stock solution FTIR spectra obtained using CaF_2 windows.*

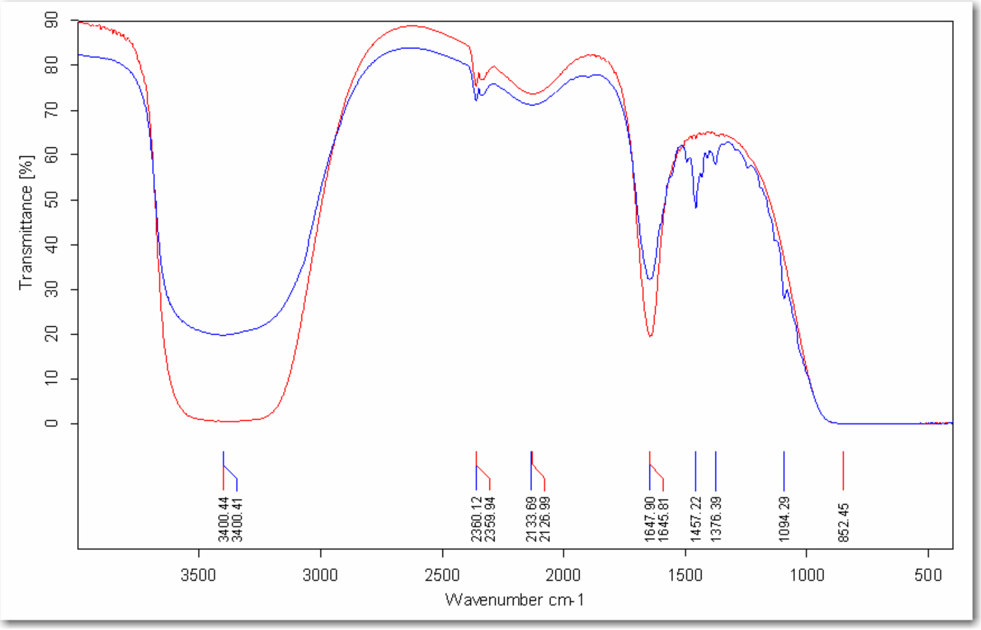
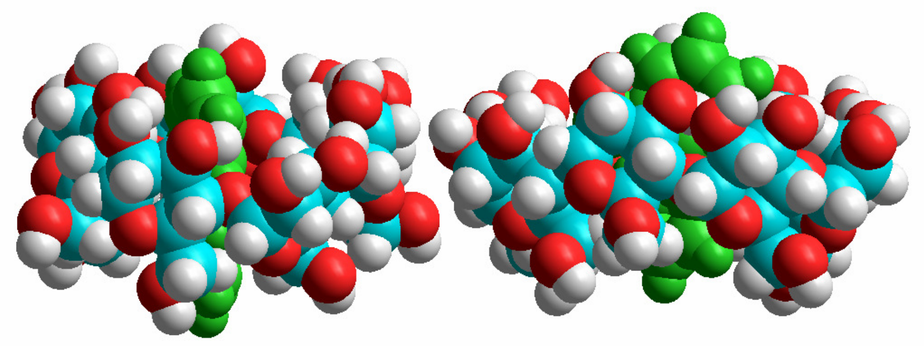


Fig. 4 *FTIR spectra of solutions containing PCB/β-CD/H2O (blue) and PCB/H2O (red) obtained using CaF_2 windows.*

The argument on the interaction between the partners is based only on observed decrease of the band intensity characteristic to C=C aromatic vibration (1647.90÷1645.81 cm^{-1}) of PCB due to cyclodextrin presence in ternary system. The PCBs migrate in the β-CD solution which is evident in the shown spectra. Both range restrictions mentioned above, affect the possibility to discern the mode of interaction of different PCB present in analyzed mixture.

Structures with PCB dipole moment oriented parallel and anti-parallel with the CD axis b (small base)-B (big base) were calculated to discern the polarity role on the interaction.



2PCB- βCD b 3PCB-βCD B

Fig. 5 *Structures of 2PCB b and 3PCB B with βCD.*

Table 1 *Interaction energies of PCB-βCD and PCB-γ CD (kcal/mol)*

Complex	2PCB-βCD B	2PCB-βCD b	2PCB-γCD b	2PCB-γCD B	22'PCB-βCD B	22'PCB-γCD B
Interaction energy	–58.13	–22.42	–24.93	–24.91	–48.56	–27.57
Ebond	–1.88	–0.48	–0.51	–0.76	–2.01	–0.92
Eangle	8.97	–2.49	–2.06	–0.64	9.10	–0.48
Etorsion	–11.10	2.82	–6.43	–9.20	–6.95	–9.23
EvdW	–43.79	–22.20	–15.30	–15.60	–45.16	–17.94
Estr-bond	1.052	–0.08	–0.06	–0.01	0.98	–0.06
Eelectrostatic	–11.38	0	0	1.3126	–10.33	1.06

Table 2 *Interaction energies of PCB-βCD and PCB-γ CD (kcal/mol)*

Complex	22'3PCB-βCD B	22'3PCB-βCD b	22'3PCB-γCD B	22'3PCB-γCD b
Interaction energy	–23.59	–23.59	–27.89	–27.76
Ebond	–0.34	–0.34	–1.07	–1.07
Eangle	–2.75	–2.75	–2.30	–2.13
Etorsion	3.22	3.24	–6.47	–5.49
EvdW	–23.72	–23.74	–18.48	–19.48
Estr-bond	0.01	0.01	–0.10	–0.03
Eelectrostatic	0	0	0.54	0.44

The most stable complexes are those with gamma cyclodextrins, as expected (the complexes with the electrostatic term differing of zero, terms are not considered here because in the calculation were used structures optimized with the AM1 method). The wan der Waals (vdW) interaction has the biggest weight in the complexes stabilization. The most stable complexes are formed when the chlorine atoms are oriented toward the B base because the repulsive interaction between Cl and O is minimized.

4. Conclusion

The interaction between β-CD and PCBs mixture, extracted from transformer oil, was probed by the FTIR spectral study. Information on the PCB's-CD's mode of interaction and complexes stability were obtained from the molecular mechanics study.

Acknowledgement: Authors are thankful to Professor dr. Mihaela Hillebrand, Senior researcher Constantin Toader for providing the compounds and Prof. Ghe. Surpateanu from the University of Dunkerque for the computational resources.

REFERENCES

1. Erikson, M.D. (1986) **Analytical Chemistry of PCB**, Butterworth Publisers, Boston.
2. Schultz, D.E, Patrick, G. and Duinker, J.C (1998) *Env. Sci, Technol*. **23**, 852-9.
3. Doremenq, P., Guillano, M. and Mille, G. (1992) *Talanta* **39**, 149-54.
4. Hembree, D.M, Smyrl, N.R, Davies, W.E. and Williams, D.M. (1993) *Analyst* **118,** 249-52.
5. Gurka D.F, Pyle S.M. and Farnham, I. (1991) *J. Chrom. Science* **29**, 339-44.
6. Busch, B. and Barnard, E.L. (1995) *Archiv Env Contam. Technol* **29**, 322-6.
7. Krupcik, J, Majekova, M., Majek, P., Hrousek, J., Benicka, E., Onusca, F., Sandra, P. and de Zeeuw, J. (1995) *Fresenius J. Analyt. Chem*. **352**, 696-8.
8. Chiosa, V., Done, R., Mandravel, C., Mindrila, G., Toader, C. and Stanculescu, I. (2008) *Book of Abstracts* 6th Int Conf. Chem. Soc. SE Europe Countryes, 10-14 september, Sofia, Bulgaria, 325.
9. Padington, I.S. (1987) *Chemistry in Britain* **23**, 445.
10. Mandravel, C. and Chiosa, V. (2005) **Metode de studiu ale structurii moleculare**, Ed. Univ. Buc., 149-50, 227-33.