Effects of different solvents on ultraviolet absorption and fluorescence intensity of 2,4-dichlorophenol, 2,4,6-trichlorophenol and Pentachlorophenol

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Abstract. In order to study the influence of the UV-visible absorption spectra and fluorescence spectrum from 2,4-dichlorophenol (2,4-dcp), 2,4,6-trichlorophenol (2,4,6-tcp) and pentachlorophenol (ptcp) in different solvents. Using methanol, tetrahydrofuran (THF), ethanol, dimethyl sulfoxide (DMSO) and acetone solvent models, computer simulation prediction and analysis of the three chlorophenols were carried out. It provides a reference for the choice of solvents in the determination of chlorophenols by the Ultraviolet-Vis absorption spectrophotometry and fluorescence intensity detection.

1. Introduction
As aromatic organic compounds, chlorophenols generally have strong toxicity and are difficult to explain in nature[1]. At the same time, aromatic organic compounds have good bioaccumulation, environmental stability and biological toxicity[2]. 2,4-dcp, 2,4,6-tcp and ptcp are difficult to degrade, highly toxic and have teratogenic, carcinogenic and mutagenic effects[4, 5]. Therefore, it is very important to determine the properties of its chlorophenols, which are commonly used in Ultraviolet-visible (UV-Vis) absorption spectrum analysis and molecular fluorescence spectrum determination. Due to the close relationship between the spectral method and the solvents used, the UV-Vis Absorption Spectra and fluorescence intensity of chlorophenols in different solvents are different[6-8]. Especially in quantitative determination, the UV-Vis absorption and fluorescence intensity of chlorophenol are directly affected. If the solvents selected are not suitable, it may directly affect the determination, especially affect the detection sensitivity and detection limit[9, 10]. With the rapid development of computer chemistry, computer simulation can replace the conventional experimental results, and the results of computer simulation can provide important basis for experimental research[11-13]. In this study, several solvents were selected, I.E. water, methanol, tetrahydrofuran (THF), ethanol, Dimethyl sulfoxide (DMSO) and acetone, to treat 2,4-dcp, 2,4,6-tcp and ptcp in UV-Vis absorption spectra and fluorescence intensity spectra were calculated and analyzed, and in order to provide reference for the choice of solvent for the UV-Vis absorption of chlorophenols, the absorption of chlorophenols in vacuum model was compared with that in the same calculation level.
2. Research methods
Quantum view and molecular software Gauss-view were used to construct molecules of 2,4-dcp, 2,4,6-tcp and ptcp. Perform structural optimization calculations in the B3LYP[14-16]/6-311G*[17] basis set in the quantum computing software, and check the stability of the optimized structure through the infrared vibration frequency, and use it in water, methanol, ethanol, propanol, THF and DMSO and other solvents. Calculate the UV-Vis and fluorescence absorption of 2,4-dcp, 2,4,6-tcp and ptcp under the vacuum model with the same calculation level, The UV-Vis absorption value and fluorescence intensity of 2,4-dcp, 2,4,6-tcp and ptcp were compared with each other, and the influence of each solvent model on UV-Vis absorption and fluorescence intensity were analyzed.

3. Research results and analysis
3.1. Structural configuration
The structure optimization calculation was performed on the B3LYP/6-311G* basis set, and the optimized molecular structure diagrams of 2,4-dcp, 2,4,6-tcp and ptcp, there are all the atoms of chlorophenols are in the same plane.

3.2. Infrared vibration
Under the same calculation basis set, the structurally optimized 2,4-dcp, 2,4,6-tcp and ptcp are further calculated for the infrared spectrum vibration frequency, as shown in Figure 1. There was no negative in the value, and it can be seen that there was no false frequency in the vibration, indicating that the optimized structures of 2,4-dcp, 2,4,6-tcp and ptcp exist stably[19]. Due to the difference in the number of Cl atoms in the chlorophenol aromatic ring, it can be seen that the peaks generated by the vibration and swing of the aromatic ring’s fixed frame have obvious differences. 2,4,6-tcp and ptcp have obvious oscillation peaks of O-H atoms at 424 cm\(^{-1}\), but do not appear in 2,4-dcp. This is because compared with 2,4,6-tcp and ptcp, the O-H swing peak in 2,4-dcp has a certain red shift, which cannot be shown in figure 1. As for the characteristic absorption peak of each chlorophenol, the O-H stretching vibration value in 2,4-dcp is obviously smaller than that in 2,4,6-tcp and ptcp, and the wave number is larger, and relative to 2,4,6-tcp and ptcp stretching vibration red shift. The reason is that 2,4-dcp has less functional group Cl than 2,4,6-tcp and ptcp, and its total chlorine atom has a weak electron withdrawing effect, which makes the reduction of benzene ring charge density small. The electron transfer in the phenolic hydroxyl group to the aromatic ring is less, the charge density between O-H is higher, and the O-H bond is stronger.

![Figure 1. Infrared absorption spectra of the chlorophenols.](image)
3.3. Charge distribution
The Mulliken charge distribution calculations are carried out on the C atoms in the aromatic rings and O atoms and Cl atoms in the phenolic hydroxyl group of 2,4,6-tcp, 2,4,6-tcp and ptcp. The results are shown in Table 1. With the electron withdrawing effect of 5 Cl atoms in ptcp, the charge density of each C atom in the aromatic ring is increased, and the electronegativity is strengthened. At the same time, the electronegativity of the O atom is weakened, and the force with the H in the phenolic hydroxyl group is reduced, and the OH stretches vibration is stronger, consistent with infrared vibration results.

|         | 2,4-dep | 2,4,6-tcp | p tcp | 2,4-dep | 2,4,6-tcp | p tcp |
|---------|---------|-----------|-------|---------|-----------|-------|
| 1-C     | 0.392   | 0.549     | -0.568| O       | -0.594    | -0.576| -0.571|
| 2-C     | -0.362  | -0.374    | -0.260| 2-Cl    | 0.039     | 0.057 | 0.116 |
| 3-C     | 0.064   | 0.087     | -0.128| 3-Cl    | \         | \    | 0.108 |
| 4-C     | -0.314  | -0.326    | -0.140| 4-Cl    | -0.009    | 0.010 | 0.105 |
| 5-C     | -0.025  | 0.089     | -0.124| 5-Cl    | \         | \    | 0.110 |
| 6-C     | -0.149  | -0.366    | -0.246| 6-Cl    | \         | \    | 0.007 | 0.061 |

3.4. Ultraviolet visible absorption spectrum
Using water, methanol, THF, ethanol, DMSO and acetone as solvents, respectively, 2,4-dep, 2,4,6-tcp and ptcp are calculated under the same calculation basis. The corresponding UV absorption spectra are shown in figure 2a, b and c. They are 2,4-dep, 2,4,6-tcp and ptcp’ UV absorption spectra in models such as in vacuum, water, methanol, THF, ethanol, DMSO, and acetone, respectively. It can be seen clearly in figure 3a that water, methanol, THF, DMSO and acetone all make the UV-Vis absorption value improved. Among them, the DMSO is the most obvious, and the UV-Vis absorption peak has a more obvious red shift. While in ethanol solvent, the absorption peak is significantly reduced. At the same, it can be seen clearly in figure 3b that water, methanol, THF, DMSO, and acetone all make the absorption peak increase to a certain extent, and the effect of DMSO is the most obvious, each solvent makes the ultraviolet absorption peak red-shift. While the UV-Vis absorption peak in the acetone solvent is significantly reduced. However, it is obvious in figure 3c that in various solvent models, the UV-Vis absorption peak is significantly improved, and there is no obvious difference in solvent increase. This may be affected by the relatively high polarity of 2,4-dep, while the polarity of 2,4,6-tcp and ptcp is low, and ptcp is simultaneously absorbed electrons by five chlorine atoms[19].

Figure 2. UV-Vis absorption spectrum of the chlorophenols.
3.5. Fluorescence intensity spectrum

Using water, methanol, THF, ethanol, DMSO and acetone as solvents, 2,4-dcp, 2,4,6-tcp and ptcp are calculated under the same calculation basis set. The corresponding fluorescence intensity spectra are shown in Figure 3 d, e, and f, which represent the fluorescence intensity spectra of 2,4-dcp, 2,4,6-tcp and ptcp in each solvent, respectively. It is obvious from the figure that 2,4,6-tcp and ptcp produce weaker fluorescence in each solvent, and there is no obvious difference in fluorescence wavelength and intensity. However, 2,4-dcp produces strong fluorescence in different solvents. The fluorescence patterns of each solvent are similar, and there are two fluorescence peaks. The stronger fluorescence is at about 226nm, and the second-stronger fluorescence value is at about 270nm. And the corresponding solvents for 2,4-dcp to produce fluorescence intensity from strong to weak are water, methanol, ethanol, acetone, DMSO and THF. This may be because trichlorophenol and ptcp have more chlorine atoms than dichlorophenol, which destroys the large π-bond structure of the benzene ring[20].

![Figure 3. Infrared absorption spectra of the chlorophenols.](image)

4. Conclusion

Among the six solvents of water, methanol, THF, ethanol, DMSO and acetone, the DMSO solvent enhances the UV-Vis absorption effect of 2,4-dcp and 2,4,6-tcp. DMSO is the first of several solvents when doing UV-Vis -visible absorption spectroscopy for the chlorophenol. At the same time, there is no obvious change in the fluorescence spectrum intensity of each chlorophenol in each solvent. The fluorescence intensity of 2,4,6-tcp and ptcp in each solvent is extremely weak, and it is not suitable for quantitative detection of them by fluorescence. However, 2,4-dcp has good fluorescence intensity in various solvents and is suitable for quantitative detection, especially in two solvents, water and methanol.

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