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Experimental and theoretical analysis of substituent effect on charge transfer complexes of iodine and some alkylbenzenes in n-hexane solution at 303 K



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ABSTRACT

The charge transfer (CT) interactions in n-hexane solutions containing iodine (acceptor) and aromatic compounds, benzene (BEN), toluene (TOL), *o*-xylene (OXYL), *m*-xylene (MXYL) and mesitylene (MESI) were investigated by ultrasonic, UV-Visible spectroscopic methods and DFT analysis. The trend in acoustical and excess properties with molar concentration in these systems established the existence of strong solute–solute interaction and formation of CT complex between iodine and the five aromatic compounds. Computed interaction energy values in the present investigation confirmed the formation of CT complex in these systems. Both the experimental methods and theoretical investigation of these systems indicated that tendency for formation of CT complex increases with increase in the number of methyl substituent in the aromatic ring. Our computed results are in good agreement with the experimental observations.

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Specifications Table

Subject area	Organic Chemistry, Charge transfer complexes
Compounds	CT complexes of iodine with five alkylbenzenes (benzene, toluene, o-xylene, m-xylene and mesitylene)
Data category	Ultrasonic scan , Spectral
Data acquisition format	Ultrasonic scan using interferometer, UV-visible spectrophotometer
Data type	Analysed and simulated
Procedure	The charge transfer (CT) interactions in n-hexane solutions were investigated by ultrasonic and UV-Visible spectroscopic and DFT analysis. Formation constants for the five systems are reported. Computed interaction energy values in the present investigation confirmed the formation of CT complex in these systems. Both the experimental methods and theoretical investigation of these systems indicated that tendency for formation of CT complex increases with increase in the number of methyl substituent in the aromatic ring.
Data accessibility	Data is with the article

1. Rationale

When iodine and benzene derivatives are dissolved in a non-polar solvent, an electronic absorption not present in the spectra of either compound is observed and a color change is noticed [1,2]. Mulliken attributed this to CT complex formation and the new band corresponding to electronic transitions from HOMO of molecules of benzene derivatives to the LUMO of iodine [3]. This charge transfer peak may be easily excited in an elective manner and hence the benzene-iodine complex has become useful classic model for studying the kinetics of charge transfer reactions [4–7]. Extensive work has been done in the past years in studying this system in the solution phase [8,9]. Cheng et al. identified 1:1 and 1:n benzene-iodine and similar complexes through femtosecond pump-probe experiments which was identified by mass spectrometry [10,11]. The formation of CT complexes with halogens and several homocyclic aromatic compounds was established by UV spectroscopy [12–15]. The most basic halogen, iodine can form CT complexes with electron donors like aromatic hydrocarbons. CT complexes have received much attention among researchers in the recent years due to their wide applications in the field of biological, crystal engineering and drug-action mechanism [16–20]. Detection and characterization of such kind of non-covalent interactions is very helpful in understanding the fundamental origin of the biological and chemical processes [21–24]. The influence of substituents in the aromatic ring on the stability of these complexes was investigated using IR, NMR and UV-visible spectral techniques [25–26]. The potentiometric titration in conjunction with constant activity method has been used to determine association constants of iodine complexes with some donors and with some drugs [27]. In recent years, the acoustical investigations have been successfully employed in the detection and determination of the stability constants of CT complexes. The thermodynamic properties of several CT complexes and hydrogen bonded complexes were also well established [28–30]. The formation of CT complexes between iodine (acceptor) and certain heterocyclic compounds (donors) has been investigated by ultrasonic and UV-visible spectral methods in dimethyl sulfoxide (DMSO) medium by Ulagendran et al. They found that both spectral and ultrasonic methods yielded similar association constant values for CT complexes [31]. Electronic structure calculations have been carried out in conjunction with experimental analysis to ascertain the most stable geometry conformation of benzene-iodine complex [32,33]. Previous reports on spectroscopic and theoretical studies revealed the geometry of CT complexes between benzene and halogens [34–36]. Fredin and Ferguson suggested the existence of the axial structure of benzene-iodine complex in a nitrogen matrix through IR experiments [37–40]. Both the density functional theory (DFT) based calculations and ab initio calculations by Mebel et al. pointed out that the most stable geometry for benzene-iodine CT complexes is the above-bond conformation and not the axial type [41–42]. This paper deals with the study of charge transfer (CT) interaction between iodine and five aromatic hydrocarbon molecules by ultrasonic and UV-Visible spectroscopic techniques. The DFT analysis of these complexes also performed to ascertain the geometries of these five complexes and to determine the interaction energies.

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