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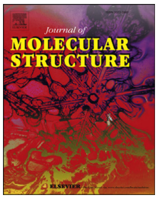

Influence of fused aromatic ring on the stability of charge transfer complex between iodine and some five membered heterocyclic molecules through ultrasonic and spectral studies

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ABSTRACT

The charge transfer (CT) interaction between two fused heterocyclic compounds with basic pyrrole group as donors, viz., indole (IND) and carbazole (CAR), and iodine (acceptor) in DMSO medium is investigated by ultrasonic and UV–visible spectral methods at 303 K. The formation of CT complex in these systems is established from the trend in acoustical and excess thermo acoustical properties with molar concentration. The frequency acoustic spectra (FAS) is also carried out on these two systems for two fixed concentrations 0.002 M and 0.02 M, and in the frequency range 1 MHz-10 MHz to justify the frequency chosen for ultrasonic study. The absorption coefficient values in solution are computed and discussed. The formation constants of these complexes are determined using Kannappan equation in ultrasonic method. The formation of 1:1 complexes between iodine and IND, CAR was established by the theory of Benesi – Hildebrand in the UV–visible spectroscopic method. The stability constants of the CT complexes determined by spectroscopic and ultrasonic methods show a similar trend. These values also indicate that the presence of fused aromatic ring influences significantly when compared with K values of similar CT complexes of parent five membered heterocyclic compound (pyrrole) reported by us earlier.

1. Introduction

Iodine is a σ-type acceptor and it has large molecular polarizability among halogens. Iodine forms large number of molecular charge transfer complexes with several aromatic, aliphatic and heterocyclic compounds [1–5]. Investigation of CT complexes of iodine and several donors has played important role in the development of theories of molecular association. It has been found that excitation of I_2–aromatic charge transfer band facilitates formation of the transition state for addition of halogen to aromatic compounds [6]. Iodine also forms 1:1 CT complexes with drugs like esmolol, famotidine, lansoprazole and oxprenolol. There is decrease in intensity of iodine band during the complex formation and also there is simultaneous appearance of blue shift band. This provides an efficient method for the estimation of drugs from the intensities of iodine and blue shift band [7]. There are known biologically active fused aromatic systems containing pyrrole group in natural products, namely, alkaloids or synthetic drugs containing in their structure indole and carbazole moieties [12–17]. These compounds possess anti-cancer, antibacterial, antifungal, anti-inflammatory, hepatoprotective, anti-HIV and antiprotozoan properties [8–17]. They can also be estimated by the CT complex formation with iodine.

Charge-transfer complex formation between two molecules involves the transfer of an electron from the HOMO of the donor to the LUMO of the acceptor. Iodine is electron acceptor and hence the CT complex formation is due to electrophilic interaction between iodine and donor molecules. Pyrrole, indole and carbazole give different products in electrophilic substitution reactions. Pyrrole gives mainly 2-substituted product while indole gives a mixture of 3- and N- substituted products in trifluoroacetylation reaction. Carbazole forms exclusively N-substituted product in the same

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reaction under similar conditions [18–20]. Recently, the formation of charge transfer and hydrogen bonded complexes have been successfully detected by acoustical and UV VIS. spectroscopic methods and the structural and temperature effect on the stability of the complexes have been discussed on the formation of constants obtained by both these methods [21–24]. Further, we have reported [25] the formation of CT complexes between iodine and some five membered heterocyclic aromatic compounds containing single hetero atom and the formation constants were determined in DMSO medium by ultrasonic and UV–visible spectral methods. The formation constants of complexes of iodine with the heterocyclic aromatic compounds depend on the structure of the donor molecules. In this paper, we report the results of CT complexes of iodine with indole and carbazole in DMSO medium obtained through ultrasonic and UV- visible spectroscopic methods at 303 K. This study is made with the main aim to investigate the influence of fused aromatic ring in pyrrole system on the formation constants of CT complexes of the two molecules with iodine.

2. Experimental

Analar grade samples of indole (>99%, Lancaster, England) and carbazole (>99%, Merck, Mumbai) were used as such. The solvent dimethyl sulphoxide (S.D. Fine Chemicals Pvt. Ltd, Mumbai) was purified by standard procedures before use [26,27]. The ultrasonic velocity ‘u’ of pure liquids and ternary mixtures was measured with a multi frequency ultrasonic interferometer (Model-M83 of Mittal Enterprises, New Delhi). In the present work, a steel cell fitted with a quartz crystal of 3 MHz frequencies was employed with accuracy of 0.1 ms^{-1}. The instrument was calibrated by measuring the velocity of triple distilled water, carbon tetrachloride at 298 K and dimethyl sulfoxide at 303 K and these values are comparable with literature values [28,29]. A 10 ml specific gravity bottle and a single pan digital balance of Shimadzu made with an accuracy of $\pm 10^{-6}$ g were used to determine the density of the solutions. Ostwald's viscometer was used to find the viscosity, in which the flow time for solutions was measured through a digital stop clock of accuracy ±0.01 s. In all cases, the experiments were performed generally at least in six replicates for each composition and the results were averaged. The reproducibility in mole fraction was within ±0.0002 units. The temperature of the samples was maintained constant to an accuracy of ±0.1 K by digitally controlled thermostatic water bath. UV–visible spectra were recorded on a Shimadzu UV-1650 model spectrophotometer with quartz cell of 1 cm optical path length. The solvent DMSO was used for the base line correction. The absorbance spectra were recorded in the wavelength region of 200–700 nm at the scanning rate 0.2 nm/s and a slit of width 1 cm.

The acoustical and excess thermo acoustical properties in the ternary mixtures were computed from the measured values of ultrasonic velocity (u), density (ρ) and viscosity (η) using the standard formulae reported in the literature [30]. The stability constants of the complexes were calculated from the experimentally determined ‘u’ values by employing Kannappan equation [28] and from the absorbance values of UV–vis spectra by employing Benesi–Hildebrand equation [31].

3. Results and discussion

Indole does not have strong electron donor properties as found by Pullmans from the orbital energies by quantum mechanical calculations [32,33]. They showed that indole can act only as fair electron donor. Iodine molecule being a more polarizable and fairly good electron acceptor can form CT complexes with indole derivatives [34]. Charge transfer will occur only if there is overlap between the donor and the acceptor orbitals. At room temperature, in solution, thermal agitation may keep the two molecules apart. It may be necessary to force the donor and acceptor molecules to study the charge transfer. This can be done by dissolving both substances in suitable solvent and freeze the solution, whereby the solvent crystallizes out leaving the solutes in close proximity [34]. Carbazole with larger number of π-electrons can also form CT complex with iodine. This paper deals with the study of influence of fused rings in pyrrole system on the stability of CT complexes of indole and carbazole with I_2 in DMSO solution.

3.1. Acoustical parameters

The measured ultrasonic velocity (u), density (ρ) and viscosity (η) for the two ternary systems at various concentrations are summarized in Table 1. Fig. 1(a) contains the plots of ultrasonic velocity against concentration of donor which is equal to that of acceptor. A close look at the plots in Fig. 1(a) and the measured parameters in Table 1 reveals that the ultrasonic velocity decreases with increase in concentration of components in the two systems and the variation is non-linear. Normally polar solvents provide the medium and dilution for the mixture, which in turn minimizes the solvent – solute interaction. This is also supported by the slight increase in density with concentration in both the systems. The variation of ultrasonic velocity with concentration of solute molecules may be attributed to solute-solute interactions. In both the systems the rupture of self -association of polar component (IND and CAR) molecules may be dominant over the solute - solute interactions that lead to the decreasing trend in ‘u’ at higher concentrations. The decrease in the ultrasonic velocity with concentration may be an indication of specific molecular interactions such as dipole-dipole or complex formation [25]. This decreasing trend with concentration suggests that the non -covalent interactions are weak. The computed acoustical parameters for the two ternary systems in DMSO medium at 303 K are listed in Table 2. Adiabatic compressibility (κ) is used to assess the molecular interactions and the structural aspects of components involved in liquid mixtures. Generally, increase in κ value indicates weak association of solute molecules, structure breaking behavior and rarefied behavior of the system while decrease in κ value suggests dominance of strong attractive forces. An inspection of the variation of κ values with concentration in Table 2 for the two ternary systems suggests that the structure of donor molecules determine the magnitude of ‘κ’. The molecular compactness is more in indole system than in CAR system. This may be due to difference in the site of complex formation in the two heterocyclic aromatic molecules. In CAR molecule, the pyrrole ring is fused by two aromatic rings while in IND system there is only one aromatic ring fused to pyrrole system. For a particular system the ‘κ’ values increase with increase in concentration. This may be attributed to the structure breaking behavior and the rarified nature of the system as evidenced through the behavior of ‘u’. It is observed that the free length follows the similar trend as similar to that of ‘κ’. The slight increase in the value of L_f with concentration also indicates that weak molecular association exists in the two systems. It is interesting to analyze the data for internal pressure and free volume for the two ternary systems (Table 2). Generally, π_i and V_f follow similar trend as ultrasonic velocity and adiabatic compressibility respectively. It is found that the ‘π_i’ values at a particular concentration is higher for IND system than that for CAR system. Further ‘π_i’ decreases with increase in concentration in the two systems (Fig. 1(b)). This suggests that in IND system the intermolecular interaction appears to be stronger than in CAR system. The decreasing trend in ‘π_i’ with increase in concentration also supports the view that specific interactions may lead to the rupture of cohesion in heterocyclic aromatic compound leading to formation of monomers which