Journal of Molecular Liquids 196 (2014) 404–410

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Acoustical and spectroscopic investigation of charge transfer complexes of certain aromatic compounds with iodine in n-hexane at 303 K

R. Kumar [a], A. Justin Adaikala Baskar [b,*], V. Kannappan [c], D. RoopSingh [c]

[a] Department of Physics, The New College, Chennai 600 014, India
[b] Department of Chemistry, Loyola College, Chennai 600 034, India
[c] Department of Chemistry, Presidency College, Chennai 600 005, India

ARTICLE INFO

Article history:
Received 9 January 2014
Received in revised form 21 March 2014
Accepted 27 March 2014
Available online 8 April 2014

Keywords:
Acoustic and excess thermodynamic parameter
Formation constant
Iodine
Charge-transfer complex
Homocyclic
Heterocyclic aromatic compounds

ABSTRACT

Charge transfer complexes formed between iodine (acceptor) and six aromatic compounds, namely, benzene, pyrrole, thiophene, pyridine, quinoline and 2-methylquinoline (quinaldine) in n-hexane medium have been investigated by ultrasonic and UV–visible spectroscopic techniques at 303 K. The measured values of ultrasonic velocity, density and viscosity were used to compute acoustical parameters and excess thermodynamic parameters. The trend in acoustical parameters with concentration identifies the existence of strong interactions amongst the solutes and the sign and magnitude of excess parameters establish the possibility of complex formation between the solute molecules. The specific interaction between the solutes is identified through the UV–visible spectra using Benesi–Hildebrand theory. The formation constants (K) of the charge-transfer complexes were determined by the Benesi–Hildebrand equation (spectroscopic method) and compared with those obtained by Kannappan method (ultrasonic). The trend in K values obtained by ultrasonic and spectral methods is similar and is explained with the structures of the donor molecules.

1. Introduction

The intermolecular interactions influence the structural arrangement in liquid mixtures and such specific interactions may lead to complex formation. The influence of structure of molecules on the strength of these interactions can be detected through the simple and low cost ultrasonic method [1–6]. It is significant to investigate the formation of charge-transfer complexes because they show a variety of interesting physical properties [7–10]. The complex formation has been interpreted in terms of the association equilibrium constant and thermodynamic parameters. Charge-transfer phenomena was introduced by Mulliken and widely discussed by Foster to define a new type of adducts [11–14]. Molecular interactions between electron donors and acceptors are generally associated with the formation of intensely colored charge-transfer complexes. Molecular charge-transfer (CT) complexes of iodine with some oxazolone derivatives (donors) have been investigated spectrophotometrically in chloroform medium by Mossalamy [15]. The formation of charge-transfer complexes between iodine and 2,6-diethylaniline (DEA) and *N*-ethylaniline in chloroform has been studied by Gogary et al. [16]. Ultrasonic measurements have been employed to detect the charge-transfer complexes between aliphatic and aromatic ketones and chloroform by Kannappan et al. [17]. The formation of complexes between iodine as σ-acceptor and some heterocyclic compounds has been investigated by ultrasonic and UV–visible spectral methods in DMSO medium by Ulagendran et al. [4]. Formation constants are reported for such compounds. This paper deals with the ultrasonic investigations on the complex formation between iodine and the six homo and heterocyclic molecules, namely, benzene, pyrrole, thiophene, pyridine, quinoline and 2-methylquinoline at equimolar concentrations in n-hexane medium at 303 K. The heterocyclic aromatic molecules can act as both π as well as n-electron donors. Acoustical parameters such as adiabatic compressibility (κ), free length (L_f), internal pressure (π_i), molar volume (V_m), free volume (V_f) and Lennard–Jones Potential (LJP) have been used to identify the molecular interactions and the complexes of heterocyclic aromatic compounds. The excess parameters such as excess velocity (u^E), excess adiabatic compressibility (K^E), excess free length (L_f^E), excess molar volume (V_m^E) and excess internal pressure (π_i^E) have been calculated and analyzed in terms of the strength of molecular interactions. The formation constants of these complexes are determined by ultrasonic and UV–visible spectral methods and compared. The trend in K values is discussed in terms of the structure of donor molecules.

2. Experimental

The donor compounds benzene, pyrrole, thiophene, pyridine, quinoline and 2-methylquinoline were samples from Sigma-Aldrich Co. Chemicals and Himedia laboratories Pvt. Ltd. The mass fraction purity of the solvent n-hexane (MERCK) is (0.992). Prior to experimental

---

[*] Corresponding author. Tel.: +91 9884652530 (mobile).
E-mail address: justinbaskar@gmail.com (A.J. Adaikala Baskar).

http://dx.doi.org/10.1016/j.molliq.2014.03.035
0167-7322/© 2014 Elsevier B.V. All rights reserved.

Table 1
Supplier, purity and analysis method of purity of compounds employed.

Compound	Source	Initial mole fraction purity	Purification method	Final mole fraction purity	Analysis method
Iodine	MERCK	0.985	Sublimation	0.998	HPLC
Benzene	MERCK	0.990	Distillation	0.997	HPLC
Pyrrole	Sigma-Aldrich	0.990	Distillation	0.996	HPLC
Thiophene	Sigma-Aldrich	0.990	Distillation	0.997	HPLC
Pyridine	Himedia Labs	0.985	Distillation	0.995	HPLC
Quinoline	Himedia Labs	0.990	Distillation	0.997	HPLC
2-Methylquinoline	Himedia Labs	0.985	Distillation	0.995	HPLC

measurements, all the liquids were used after double-distillation. The suppliers of these compounds, the purification method, final mass fraction and method of analysis of estimated purity are summarized in Table 1. All the liquid mixtures were prepared by weighing appropriate amounts of pure liquids and mixed in airtight stoppered bottles to minimize evaporation losses. The density (ρ) of the pure liquids and the ternary systems were determined using a 10 mL specific gravity bottle. The weighing measurements were made with a digital balance (Shimadzu, Japan) with an accuracy of ± 0.05 mg. The accuracy of the mole fraction was $\pm 1 \times 10^{-4}$. The ultrasonic velocities in pure liquids and their ternary liquid mixtures were measured using a single crystal variable path ultrasonic interferometer operating at 2 MHz frequency supplied by Mittal Enterprises, Model F81, with an accuracy of ± 0.1 m/s. 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 [18–20]. Viscosity measurements were made with an Ostwald's viscometer in which the flow time for solutions was measured through a digital stop clock of accuracy ± 0.01 s. The temperature of the samples was maintained constant at an accuracy of ± 0.1 K by a digitally controlled thermostatic water bath. The suppliers of these compounds, the purification method and method of analysis of estimated purity are summarized in Table 1. UV–visible spectra were recorded on a Shimadzu UV-1650 model spectrophotometer with quartz cell of 1 cm optical path length. The solvent, n-hexane was used for the base line correction. The absorption spectra were recorded in the wavelength region of 200–700 nm at the scanning rate of 0.2 nm/s and a slit width of 1 cm.

From the measured values of ultrasonic velocity (u), density (ρ) and viscosity (η) various acoustical and excess thermo acoustical parameters were calculated using the standard formulae as reported in the literature [18,19,21]. The stability constants of the complexes were computed using 'u' values by employing Kannappan equation and using the absorbance values of UV–vis spectra by employing Benesi–Hildebrand equation.

The Kannappan relation [6,17] to determine the formation constant of CT complexes in dilute solutions is given by

$$K = \mathrm{Y}/(\mathrm{b}-\mathrm{y})^2$$

where, $\mathrm{Y} = (\mathrm{a} - k^{1/2}\mathrm{b}) / (k - k^{1/2})$; in which $k = \mathrm{x}/\mathrm{y}$, 'x' and 'y' are the deviations in ultrasonic velocity from ideal behavior ($\mathrm{u}_{\mathrm{ideal}} - \mathrm{u}_{\mathrm{obs}}$) at two different concentrations 'a' and 'b' respectively. $\mathrm{u}_{\mathrm{ideal}}$ is the ultrasonic velocity of the mixture calculated from the mole fraction and ultrasonic velocities of the components using additive principle.

The formation constant of the CT complex is calculated by spectral method using the Benesi–Hildebrand equation [22] and is given below

$$[D_o]/ABS = (1/K\varepsilon[A_o]) + 1/\varepsilon$$
Or
$$[A_o]/ABS = (1/K\varepsilon[D_o]) + 1/\varepsilon$$

where $[A_o]$ is the initial concentration of the acceptor, $[D_o]$ is the initial concentration of the donor, *ABS* is the absorbance of the complex, ε is the molar absorptivity of the complex formed and *K* is the formation constant of the complex.

3. Results and discussion

In the present investigation, iodine is the acceptor and six homo and heterocyclic aromatic compounds with varying structure are employed as donors (Fig. 1). The stability constant (K) values of six CT complexes are determined accurately by two different techniques and compared. The influence of structure of donor on K values is discussed.

3.1. Acoustical parameters

The measured ultrasonic velocity (u), density (ρ), and viscosity (η) and the calculated acoustical parameters for the six ternary systems in n-hexane medium at 303 K are summarized in Table 2. The graphical representations for the variation of adiabatic compressibility (κ), free volume (V_f) and molar cohesive energy (MCE) for solutions containing equimolar concentration of solutes are depicted in Fig. 2(a), (b) and (c) respectively. An inspection of the acoustical parameters in Table 2 reveals that the ultrasonic velocity increases with an increase in the concentration of component molecules except in the pyrrole–iodine system. Normally polar solvents provide the medium and dilution for the mixture, which in turn minimizes the solvent–solute interaction.

The solvent, n-hexane is a non-polar compound which is not taking part in the complex formation with both the solutes and hence in the present investigation it is used [23]. The non-linear variation of ultrasonic velocity with concentration of solute molecules may be attributed to solute–solute interactions. The molecular association becomes high at those concentrations where velocity maximum occurs [24]. In the pyrrole–iodine system the rupture of dipolar component molecules and the weak solute–solvent interaction may be dominant over the strong solute–solute interactions that lead to the decreasing trend in

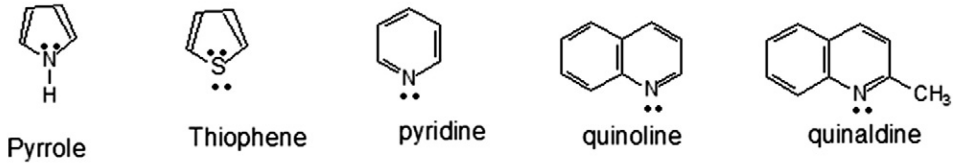

Fig. 1. Structures of heterocyclic aromatic molecules used as donors.