INTERACTION BETWEEN 1,3,5–TRITHIANE AND IODINE MONOBROMIDE IN HALOMETHANE SOTUTIONS

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Abstract : A spectrophotometric study concerning the interaction between 1,3,5-trithiane (TT) as n-donor and iodine monobromide as σ-cteptor has been performed in dichloromethane, trichloromethane and tetrachloromethane solutions at 10 °C. The results are indicative of the formation of 1:1 charge transfer complexes through equilibrium reactions in all solvents. Followed by conversion of charge transfer complex to ionic adduct in di- and trichloromethance solutions. The stability constants and ε values of complexes are obtained from the fitting of absorbance-mole ratio data in MATLAB software and in different solvents found vary in the order: CCl_4>$CHCl_3$>CH_2Cl_2 for stabilities and reverse for ε values. The rate constants of conversion of charge transfer to ionic complexes are obtained from the slops of $Ln(A_t/A_o)$ vs. t plots and found vary in the order CH_2Cl_2>$CHCl_3$. The possible reasons for the observed trends in stability constants, ε values and rate constants discussed. The contribution of dipole-dipole interactions are obtained by the semi-empirical calculations in Gaussian 98 and it was found that contribution of these forces is considerable.

Keywords: Spectophotometry, halomethanes, iodine monobromide, 1,3,5-trithiane, charge-transfer complex.

Introduction

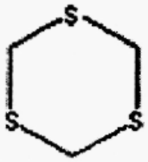
The formation of molecular complexes of charge-transfer type between electron acceptors and electron donors has been the subject of a vast number of interesting investigations [1,2]. Various aspects of charge transfer complexes have been discussed in three books which have been written by R. S. Mulliken, L. J. Andrews and R. Foster. Different approaches in each of these-book are followed [3-5].

Molecular iodine has been the most studied of halogen acceptors. Although there are many reports on molecular charge transfer complexes between different donors and iodine in the literature [6-9], not much work has been done on similar complexes of other halogens and interhalogens [10-12]. Because of its polar nature, iodine monobromide is a stronger acceptor than iodine. As such, it responds more dramatically than iodine with respect to changes in stability of its donor-acceptor complexes with changes in donor strength or solvent [13].

In continue of our studies in the field of molecular complexes [14-16], here we report the results of spectroscopic study of the complexation of 1,3,5-trithiane and iodine monobromide in halomethane solutions.

Experimental

1,3,5–Trithiane (TT) and solvents from Merck company with highest purity available were used without any further purification. Iodine monobromide (Ridel) was used as received.



1, 3, 5 – trithiane (TT)

UV–Vis spectra were recorded on a Shimadzu spectrophotometer and the absorbance measurements were made with the same instrument at 10 °C. In order to obtain UV–Vis spectra of TT in the presence of varying concentrations of iodine monobromide 3 mL of 2-6×10^{-3} M solution of TT was transferred to a thermostated quartz cell and titrated with a concentrated solution of iodine monobromide. The same procedure was followed for obtaining absorbance mole ratio data. For obtaining the spectra of iodine monobromide in the presence of varying concentrations of TT, several solutions containing constant concentration of iodine monobromide (0.05 M) and different quantities of TT were made and the corresponding spectra were recorded. The spectra were recorded immediately after preparing the solutions.

Conductivity measurements were made for 10 mL equimolar solutions (10^{-3} M) that were previously placed in a conductometric cell and thermostated at 10 °C.

Results and Discussion

Absorption spectra of 4.1×10^{-3} M solution of TT in dichloromethane in the presence of varying concentration of IBr are shown in Figure-1. As seen, upon addition of IBr two new bands are appeared at 290 and 490 nm. The 290 nm can be assigned to the formation of charge transfer complex between IBr and TT [3]. However, the 490 nm band can be assigned to the uncomplexed IBr. The absorption spectra of 2.2×10^{-3} and 5.7×10^{-3} M TT in chloroform and carbon tetrachloride are shown in Figs.2 and 3, respectively. In these spectra also the appearance of two new bands are observed. Thus, similar to dichloromethane, in these solvents also charge transfer complex is formed.

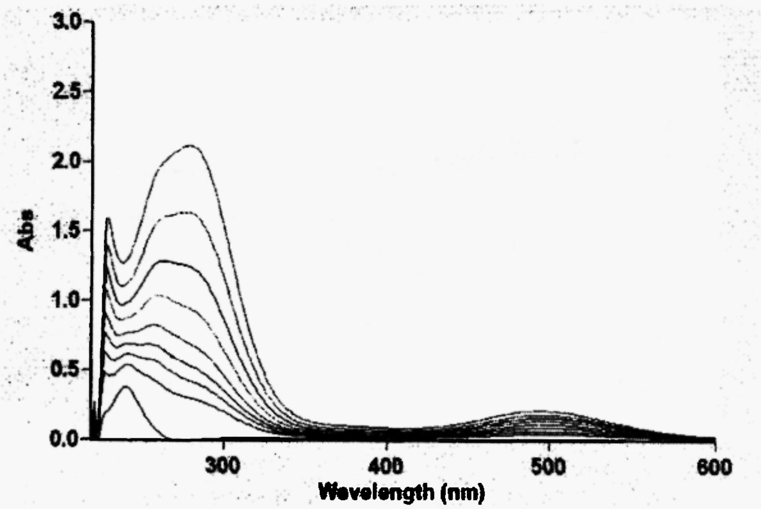


Figure-1 : Absorption spectra of 4.1×10^{-3} M solution of TT in dichloromethane solution in the presence of varying concentrations of IBr. The IBr/TT mole ratios are: 0.00, 0.17, 0.34, 0.51, 0.68, 0.85, 1.02, 1.19 and 1.36.

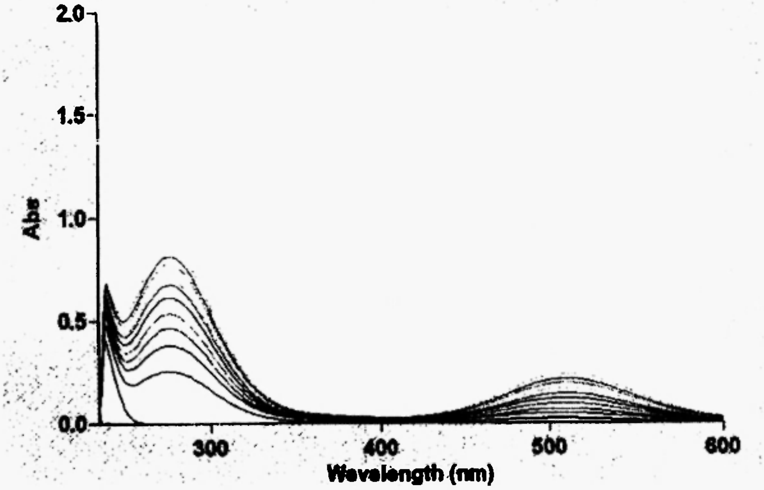


Figure-2 : Absorption spectra of 2.2×10^{-3} M solution of TT in chloroform in the presence of varying concentrations of IBr. The IBr/TT mole ratios are: 0.00, 0.17, 0.34, 0.51, 0.68, 0.85, 1.02, 1.19, 1.36, 1.53 and 1.70.

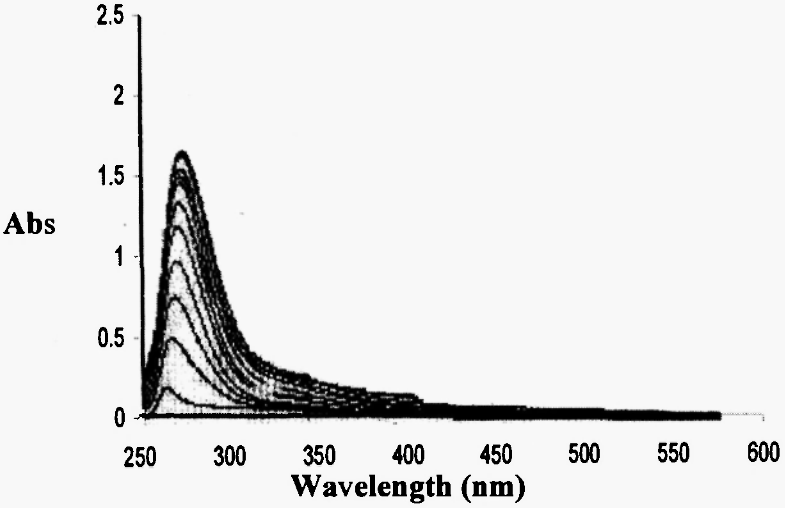


Figure-3 : Absorption spectra of 5.7×10^{-3} M solution of TT in carbon tetrachloride in the presence of varying quantities of IBr. The IBr/TT mol ratios are: 0.00, 0.17, 0.34, 0.51, 0.68, 0.85, 1.02, 1.19, 1.36, 1.53 and 1.70.

Absorption spectra of 0.05 M of IBr in dichloromethane in the presence of varying concentrations of TT are shown in Fig.4. The existence of well defined isosbestic point is indicative of an equilibrium reaction between TT and IBr [17]. Similar isosbestic points are also observed in the spectra of IBr in the presence of TT in tri- and tetrachloromethane solutions (because of similarity the corresponding spectra are not shown). Therefore, in these solvent also equilibrium reaction is occurred.

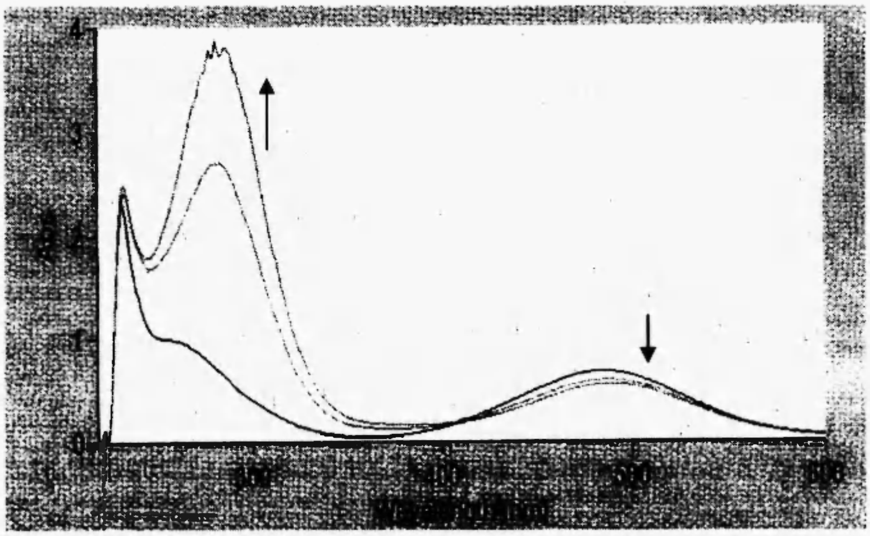


Figure-4 : Absorption spectra of 0.05 M solution of IBr in dichloromethane in the presence of varying quantities of TT. The TT/IBr mole ratios are: 0.00, 0.30 and 0.50.

Plots of absorbance vs. [IBr]/[TT] confirm the 1:1 stoichiometry in halomethane solvents [17]. Based on the spectral evidences and mole ratio results, it can be concluded the reaction of TT and IBr was performed through the following reaction.

$$TT + IBr \rightleftharpoons TT{\cdot}IBr \quad (1)$$

For evaluation of the formation constants from absorbance–mole ratio data, a nonlinear least–squares curve fitting program (curve–fitting toolbox in MATLAB) was used [18, 19]. The program is based on the iteration adjustment of calculated absorbance to the observed values. The observed absorbance of complex is given by equation (2). The mass balance equations can be written as (3) and (4) and the formation constant of the complex as (5). Substitution of equation (3) and (4) into (5) and rearrangement yields equation (6).

$$A = \varepsilon b\,[DA] \quad (2)$$

$$C_D = [D] + [DA] \quad (3)$$

$$C_A = [A] + [DA] \quad (4)$$

$$K_f = [DA] / [D]\,[A] \quad (5)$$

$$K_f\,[DA]^2\text{-}(C_AK_f{+}C_AK_f{+}1)\,[DA] + K_fC_DC_A = o \quad (6)$$

The computer fits of absorbance–mole ratio are shown in Fig.6. The good agreement between the calculated and observed values further confirms the 1:1 stoichiometry. The final logK_f and logε values in different solvents are collected in Table 1. As it can be seen, the stability constants in various solvents vary in the order: CCl_4>$CHCl_3$>CH_2Cl_2, and the logε values show the reverse trend.

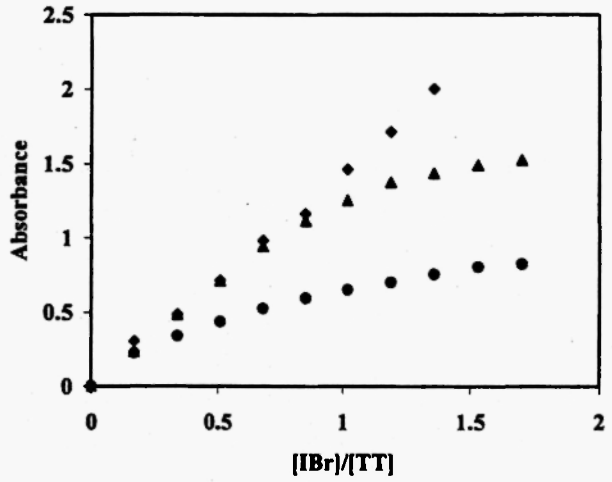


Figure-5 : Plot of absorbance vs. IBr/TT mole ratio at 300 nm in di- (♦), tri- (•) and tetrachloromethane (▲) solutions.

Table-1 : The final calculated logK, logε and logKε in halomethanes.

Solvent	**logK**	**logε**	**logKε**
CH_2Cl_2	2.10±0.04	3.49±0.02	5.60±0.06
$CHCl_3$	2.90±0.03	3.46±0.02	6.37±0.07
CCl_4	3.00±0.04	3.34+0.01	6.56+0.06

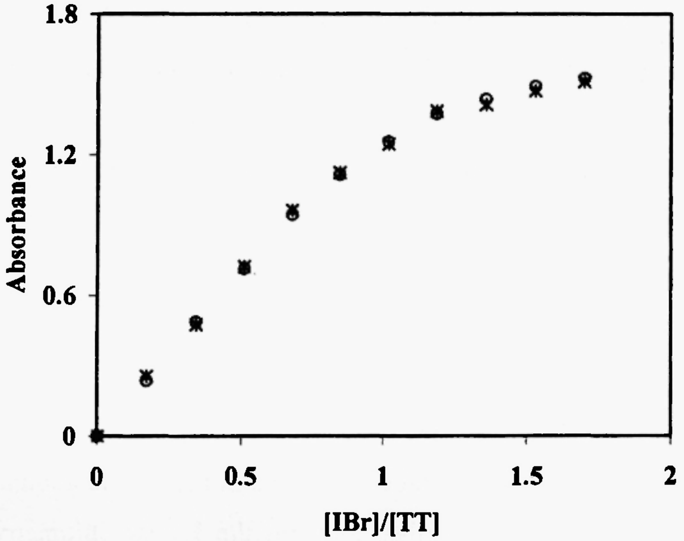


Figure-6 : Computer fitting of absorbance vs. IBr/TT mole ratio data at 300 nm in tetrachloromethane solution; (o) observed and (*) calculated points.

It is well known that solvent play an important role in the stability of charge transfer complex [3]. The calculated dipole moment of CH_2Cl_2, $CHCl_3$ and CCl_4 by Gaussian 98 are 1.504, 1.154 and 0.000, respectively [20-24]. So, the competition effect of solvent through the dipole–dipole interaction between solvent molecules and IBr or the dipole-induced dipole interaction between solvent molecules and TT will be highest in CH_2Cl_2 and lowest in CCl_4. Thus, the observation of most stability in CCl_4 and lowest stability in CH_2Cl_2 is not unexpected. Apparently, the polarity of complex is less than that of reactants. In fact, if the polarity of complex would be greater than the reactants, the reverse trend would be observed.

On the other hand, the observed trend of logε can be assigned to solvent polarity effect. With increasing of solvent polarity [25], the probability of collision of the photons to complex molecules were increased because the increasing of orientation of the complex molecules in the polar solvent. Therefore, the higher ε values were observed with increasing polarity of solvent.

It is interesting to note that by passing time, the intensity of 290 nm band was reduced gradually in CH_2Cl_2 and $CHCl_3$ solutions. Various rate equations were examined on the A-t data and it was found that there is a linear relation between the $Ln(A_o/A_t)$ vs. t data. Consequently, the initial adduct of TT and IBr interaction is further converted to another product, through a first order reaction. The k values obtained from the slope of $Ln(A_o/A_t)$ vs. t data (Fig.7) are 0.09±0.01 in CH_2Cl_2 and 0.03±0.01 in $CHCl_3$. The greater k value in CH_2Cl_2 than that of $CHCl_3$ can be related to the higher polarity of former than the latter one. It seems that the charge transfer complex is converted to ionic complex through the polarization effect of solvent. As, this effect is larger in CH_2Cl_2 than that of $CHCl_3$, the k value in the former is more than the latter. The equation due to the formation of charge transfer to ionic complex can be formulated as follows:

$$TT\cdot IBr \rightleftharpoons TTI^+Br^- \qquad (7)$$

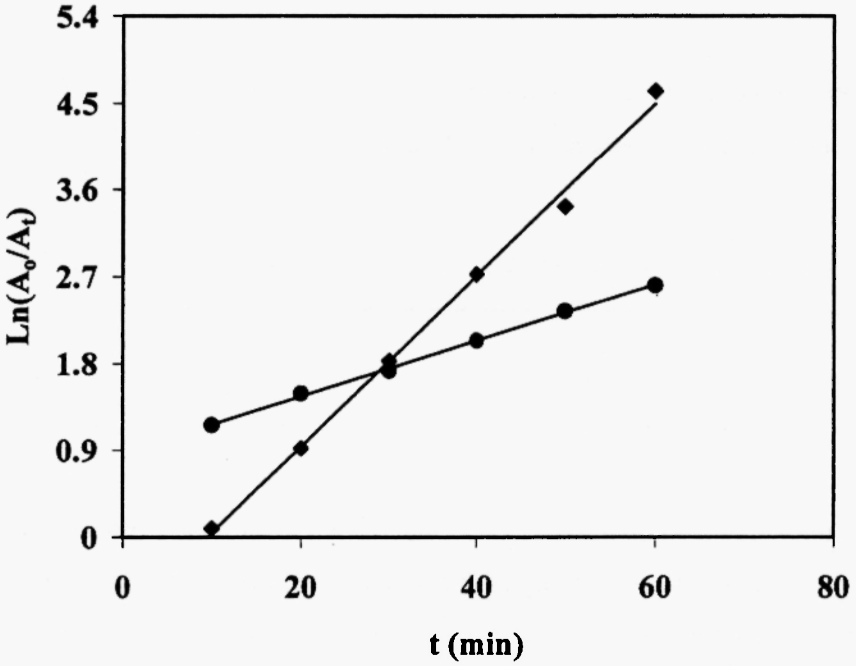


Figure-7 : Plot of $Ln(A_o/A_t)$ vs. t at 10 °C in di- (◆) and trichloromethane (•) solutions.

The above equation is further confirmed by the plot of conductance vs. time (Fig. 8). It can be seen in di- and trichloromethane solutions by passing time, the conductance increases gradually. Which indicate the ionization of TTI^+Br^- accrues through the following equation:

$$TTI^+Br^- \longrightarrow TTI^+ + Br^- \qquad (8)$$

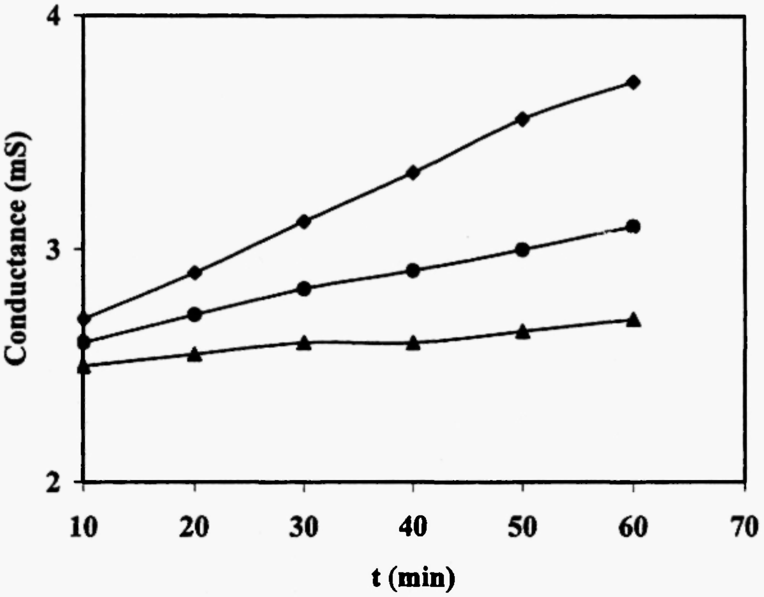


Figure-8: Plot of conductance vs. t for an equimolar mixture (10^{-3} M) of TT and IBr in di- (◆), tri- (●) and tetrachloromethane (▲) solutions.

Because of higher dielectric constant of CH_2Cl_2 (8.54) than that of $CHCl_3$ (4.806) [26], the degree of ionization in the former is more than the later one.

In order to evaluate the contribution of dipole-dipole interactions in the stability of resulting complexes the stability of complex in the gas phase was calculated by Gaussian 98. It is a connected system of programs for performing a variety of semi-empirical and ab-inito molecular orbital calculations [20]. It is capable of predicting many properties of molecules and reactions such as molecular energies and structures molecular orbitals. Also, it can serve as a powerful for exploring areas of chemical interest like substitution effects, potential energy surfaces and excitation energies. In this work, semi-empirical calculations using AMI model Hamiltonians [21, 22] with self consistent field calculations using closed shell (RHF) [23, 24] are carried out. The calculated $\log K_f$ value by this method is 3.23±0.01. The high value of $\log K_f$ value indicate that the contribution of dipole-dipole interactions in comparison of charge transfer ones is considerable.

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