INTERACTION BETWEEN BROMINE WITH TT12C4 AND HT18C6 IN DI AND TRICHLOROMETHANE SOLUTIONS

[1]Abolfazl Semnani*, [2]Ali Reza Firooz,[3]Hamid Reza Pouretedal and [3]Mohammd Hossein Kehsavarz
[1]Faculty of Sciences, University of Shahrekord, P.O. Box 115, Shahrekord, IRAN
[2]Department of Chemistry, Faculty of Sciences, University of Isfahan, Isfahan, IRAN.
[3]Department of Chemistry, Malek-e-Ashtar University of Technology, Shahin-shahr, IRAN.
e-mail: a_semnani@yahoo.com

Summary: A spectrophotometric study concerning the interaction between bromine with TT12C4 and HT18C6 has been performed in CH_2Cl_2 and $CHCl_3$ Solutions at 10 °C. The results are indicative of the formation for 1:1 macrocycle:Br_2 complex through equilibrium pathway. Following by conversion of macrocycle:Br_2 to macrocycleBr^+Br^- in nonequilibrium step. The formation constants of equilibrium steps are obtained by the fitting of absorbance-mole ratio data in MATLAB software. The rate constants of nonequilibrium step are obtained by the measurement of the slopes of $Ln(A_o/A_t)$ vs. time. The results indicate that the stabilities in $CHCl_3$ are greater than CH_2Cl_2. Also the higher stabilities of HT18C6 than that of TT12C4 complexes are observed. In the case of rate constants the reverse trend is observed for both macrocycle and solvent. The observations are discussed based on the specifications of donors and solvents.

Key words: Spectrophotometry, Thiacrownethers, Dichloromethane, Chloroform, Bromine.

Introduction

Interest in molecular complexes has long background [1] and reached the explosive stage after publication of the results of the spectrophotometric studies of H. A. Benesi and J. H. Hildebrand on iodine complexes of aromatic substances [2]. Topics Crown ethers are macrocyclic polyethers known for their ability to form stable and selective inclusion complexes with many metal ions, including alkali and alkaline such as complex geometry, complexes in relation to reaction mechanism, spectra of complexes, bonding in complexes, thermodynamics of complex formation are discussed [3].earth metal cations [4]. There has been a growing interest in the studies of molecular complexes between macrocyclic crown ethers and a variety of acceptor molecules [5-9], especially iodine [10-13]. However, to the best of our knowledge, there are only a limited number of published reports dealing with the complexation of iodine with thiacrown ethers in solution [14-16]. In the case of bromine the situation is worse [14].

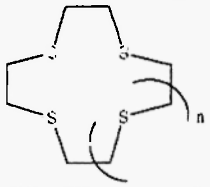
In recent years, we have been involved in the spectroscopic study of the thermodynamic and kinetics of complexation reactions of different acceptors with crown ethers in various solvents [17-24]. In this paper we report the results of spectroscopic study of complexation of bromine with TT12C4 and HT18C6 in CH_2Cl_2 and $CHCl_3$ solutions.

Experimental

Reagent grade bromine, CH_2Cl_2 and $CHCl_3$ from Merck company were used as received. TT12C4 and HT18C6 from Aldrich Company were used without any further purification except in vacuum draying.

All UV–Vis spectra were recorded on a Carry spectrophotometer and the absorbance measurements were made with the same instrument at 10 °C. The conductivity measurements were made with a Methrohm 660 conductometer with the conductometric cell thermostated at 10°C.

In order to obtain UV-Vis spectra of macrocycle upon addition of crown ethers, several 5 ml volumetric flasks were prepared and after mixing and dilution of appropriate amounts of macrocycle and bromine, the corresponding spectra were recorded. Each spectrum was recorded immediately after dilution. For obtaining UV-Vis spectra of bromine upon addition of thiacrown ether the same procedure was followed. This method also followed for obtaining absorbance vs. mole ratio data.



n=1, Tetrathia-12-crown-4 (TT12C4)
n=3, Hexathia-18-crown-6 (HT18C6)

For obtaining Job data two equimolar solutions of bromine and macrocycle made by mixing appropriate volumes of donor and acceptor solution. The absorbances were measured immediately after mixing. Kinetic data were obtained by monitoring the absorbances of 10^{-3} M bromine and 10^{-3} M macrocycle in 10 minutes time intervals.

Results and discussion

Absorption spectra of 10^{-3} M TT12C4 in the presence of varying quantities of bromine in trichloromethane solution are shown in Fig. 1. The absorption spectra in dichloromethane is similar to tricholoromethane but with higher intensity. As it can be seen a new band is appeared at 290 nm upon addition of bromine to TT12C4 solution. Neither, TT12C4 (the first spectra of Fig.1), nor bromine in $CHCl_3$ as well as in CH_2Cl_2 (Fig. 2) do not show any considerable absorption in this region. So, the observation of this band can be attributed to the formation of charge-transfer complex between bromine as σ-acceptor and TT12C4 as n-donor [25].

The corresponding spectra due to HT18C6 in trichloromethane solution (as similar to dichloromethane with higher intensity) are shown in Fig. 3 that similar to spectra of TT12C4 (Fig. 1). It can be concluded that similar to TT12C4, HT18C6 also forms charge-transfer complex with bromine. The absorption spectra of 10^{-3} M bromine in the presence of varying quantities of TT12C4 and HT18C6 in $CHCl_3$ solution are shown in Figs. 4 and 5, respectively. The observation of well defined isosbestic point is indicative of equilibrium reactions in examined solvents [26]. The similar results were obtained in CH_2Cl_2 solution.

For determination of the stoichiometry of reactions, the mole ratio and Job methods were employed [27, 28]. The corresponding plots are shown in Figs. 6-9. Despite, the mole ratio did not clearly show the 1:1 stoichiometry, the Job plots clearly confirm 1: 1 stoichiometry.

Based on spectral, mole ratio and Job evidences, it can be concluded that in both solvents macrocycles do have 1:1 equilibrium reactions with bromine. The corresponding reaction can be formulated as follows:

$$\text{macrocycle} + Br_2 \rightleftharpoons \text{macrocycle}: Br_2 \qquad (1)$$

macrocycle: TT12C4 and/or HT18C6

For the evaluation of the formation constants from absorbance mole ratio data, a non-linear least square curve-fitting program (curve-fitting toolbox in MATLAB) was used [29-31]. The program is based on the iteration adjustment of calculated absorbances to the observed values.

The observed absorbance of bromine solution at its λ_{max} is given by equation (2). The mass-balance equations can be written as (3) and (4), and the formation constant of the complex as in (5). Substitution of equations (3) and (4) into (5) and rearrangement yields (6).

$$Abs = \varepsilon\,[DA] \qquad (2)$$

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

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

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

$$K_f\,[DA]^2 - (C_AK_f + C_DK_f + 1)\,[DA] + K_fC_DC_A = 0 \qquad (6)$$

With use an approximation value for K_f, the free DA concentration, [DA], were calculated by solution of second order equation. Then, with using from data of DA concentration as x data and data of observed absorbance as y data, the least-squares fit technique is used for fitting the data. The output of this fitting is the coefficients of line fit. The coefficient of x values is ε (molar absorptivity coefficient). The obtained coefficients were used for calculation data of calculated absorbance with using of parabolic fit. To find the least-squares error, the sum of the squares of the differences between the parabolic fit and the actually data must be evaluated. Refinement of the parameter (K_f value) was continued until the sum of squares of the residuals between calculated and observed values of the absorbance for all experimental points was minimized.

A sample corresponding curve fitting are shown in Fig. 10. The good agreement between the experimental and calculated data further confirms the 1:1 stoichiometry. The final $\log K_f$ values obtained by MATLAB are given in Table 1. As seen (i) HT18C6 forms stronger complex than that of TT12C4, (ii) the stability of complexes in $CHCl_3$ is more than CH_2Cl_2 and (iii) the ε values in CH_2Cl_2 is more than the corresponding values in $CHCl_3$.

It is well known that the number of donating atoms available play an important role in the stability of the resulting donor-acceptor complexes [32,33]. Since, in the process of molecular complexation of bromine, it is reasonably assumed that the charge density is donated from the base (thiacrown ether sulfur atoms) to the antinbonding molecular orbital of bromine [34]. The increase number sulfur in the ring of HT18C6 as well as their proper spatial positions is expected to increase the crown-bromine interaction in solution.

On the other hand, the more effective completion of CH_2Cl_2 than that of $CHCl_3$ through dipole-induced dipole interactions (with bromine) and dipole-dipole interactions (with macrocycle) [35], causes that the stabilities in the former to be higher than the latter solvent. In fact, the dipole moment of CH_2Cl_2 is 1.504 Debye which is more than the corresponding value due to $CHCl_3$ (1.154 Debye) [35]. Thus, the observation of weaker complex in CH_2Cl_2 in not unexpected. Finally, the higher ε values in CH_2Cl_2 than that of $CHCl_3$ can be attributed to higher dielectric constant of former in comparison later (9.1 and 4.8 in 68 °F, respectively) [35].

It is interesting to note that by passing time, the intensity of charge transfer band at wavelength 290 nm was diminished gradually in the case both macrocycle and both solvent. The linear plots of $Ln(A_o/A_t)$ vs. time were obtained with measurements variations of aborbances of solutions in the time interval of 10 min. The obtained plots were shown in Figs. 11 and 12 for TT12C4 and HT18C6, respectively. The linear plots support the decrease of absorbances via a first order reaction. The linear relation (Figs. 11 and 12) show that the initial product of macrocycle-Br_2 interaction converts to another adduct through a first order reaction. The k values obtained from the slope of $Ln(A_o/A_t)$ vs. time plots are given in Table 2. Interestingly, the k values in CH_2Cl_2 are greater than $CHCl_3$ ones. Also, the values due to TT12C4 are greater than HT18C6.

The dipole moment of CH_2Cl_2 causes that the formation of polar complex to be facilitated in this solvent. On the other hand, the convenient fitting conditions of TT12C4 and Br^+ [36-39] promotes the faster formation of ion in the hole complex [40] in which Br^+ is located in the cavity of TT12C4. Thus, it can be concluded that macrocycle:Br_2 is converted to macrocycleBr^+Br^- through a first order reaction. Both polarity of $CHCl_3$ and fitting conditions of HT18C6 are worse than CH_2Cl_2 and TT12C4. Thus the observation of slower reactions in $CHCl_3$ solution and about HT18C6 is not unexpected.

Table 1 Calculated logK_f, logε and log$K_f\varepsilon$ values for macrocycle–Br_2 complexes in CH_2Cl_2 and $CHCl_3$ solutions.

Macrocycle	**logK_f**		**Log ε**		**log$K_f\varepsilon$**	
	CH_2Cl_2	**$CHCl_3$**	**CH_2Cl_2**	**$CHCl_3$**	**CH_2Cl_2**	**$CHCl_3$**
TT12C4	1.23±0.01	1.51±0.02	3.28±0.04	2.91±0.01	4.51±0.04	3.42±0.02
HT18C6	1.59±0.03	1.93±0.02	3.12±0.01	2.66±0.05	4.71±0.03	4.59±0.06

Table 2 Rate constants of conversion of charge transfer to ionic complexes in CH_2Cl_2 and $CHCl_3$ solutions.

Macrocycle	**k**	
	CH_2Cl_2	**$CHCl_3$**
TT12C4	0.037±0.001	0.025±0.002
HT18C6	0.015±0.001	0.008±0.001

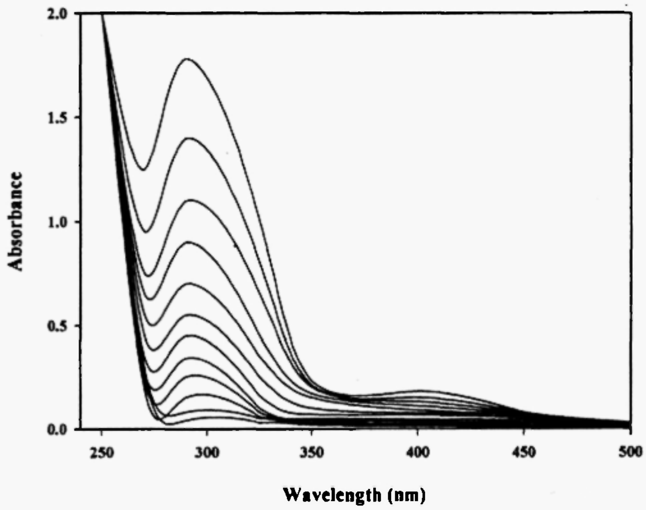


Fig.1 Absorption spectra of 10^{-3}M TT12C4 in the presence of varying quantities of bromine in $CHCl_3$ solution. The [Br2]/[TT12C4] mole ratios are:0.00, 0.17, 0.34, 0.51, 0.68, 0.85, 1.02, 1.19, 1.36, 1.53, 1.70, 1.87.

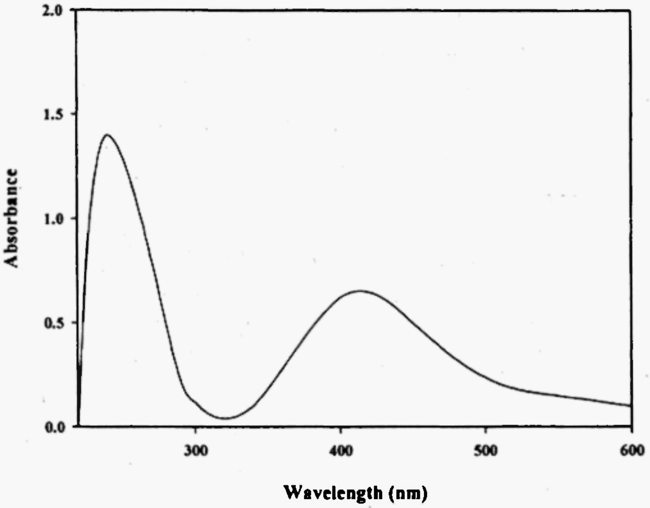


Fig. 2 Absorption spectrum of 10^{-3} M bromine in $CHCl_3$ solution.

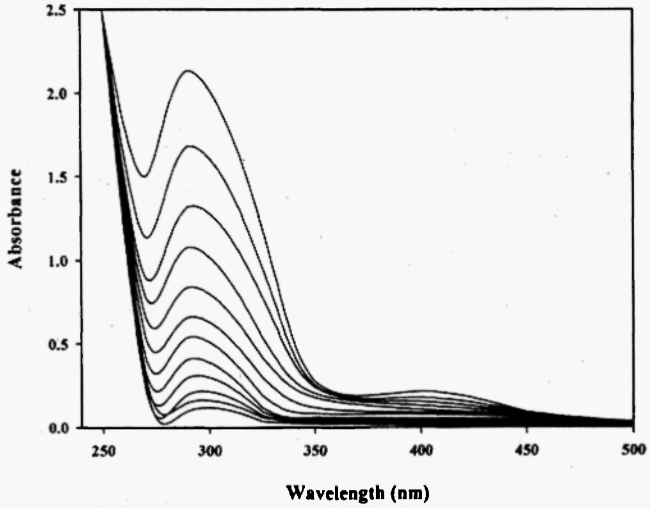


Fig. 3 Absorption spectra of 10^{-3} M of HT18C6 in the presence of varying quantities of Br_2 in $CHCl_3$ solution. The $[Br_2]/[$ HT18C6$]$ mole ratios are: 0.00, 0.17, 0.34, 0.51, 0.68, 0.85, 1.02, 1.19, 1.36, 1.53, 1.70, 1.87.

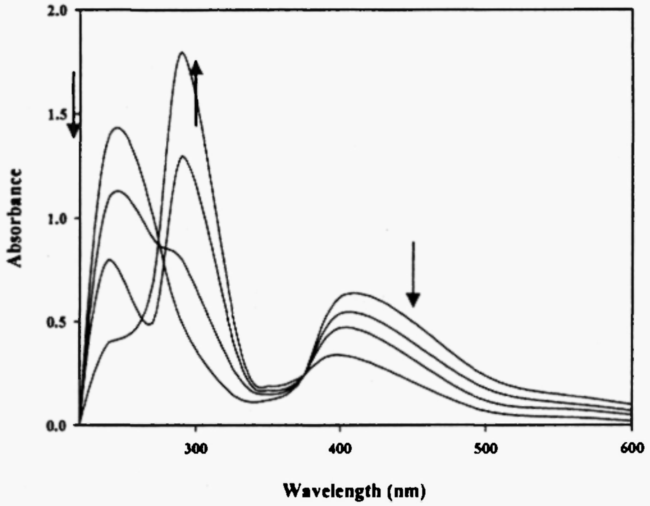


Fig. 4 Absorption spectra of 10^{-3} M bromine in the presence of varying quantities of TT12C4 in $CHCl_3$ solution. The [TT12C4]/[Br_2] mole ratios are: 0.0, 0.5, 1.0, 1.5.

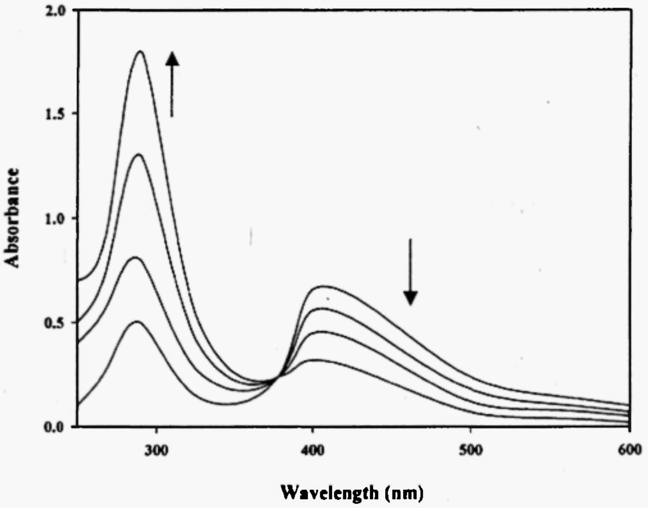


Fig. 5 Absorption spectra of bromine in the presence of varying quantities of HT18C6 in $CHCl_3$ solution. The [HT18C6]/[Br_2] mole ratios are: 0.0, 0.5, 1.0, 1.5.

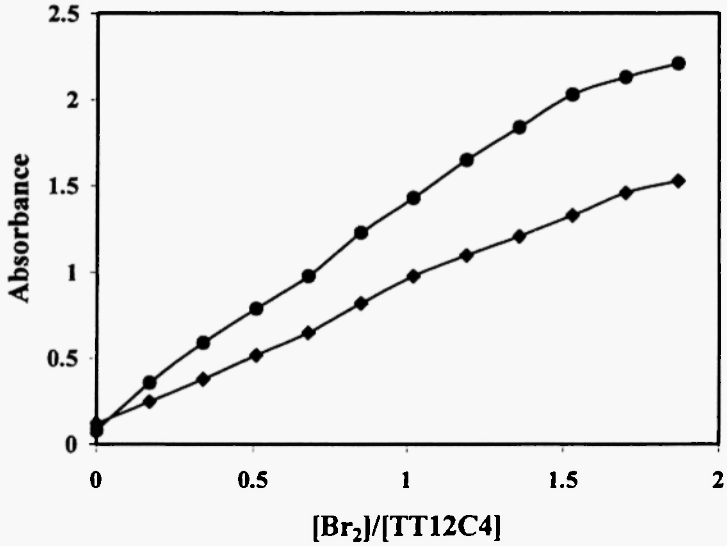


Fig. 6 Plots of absorbance vs. [Br_2]/[TT12C4] in CH_2Cl_2(•) and $CHCl_3$ (♦) solutions.

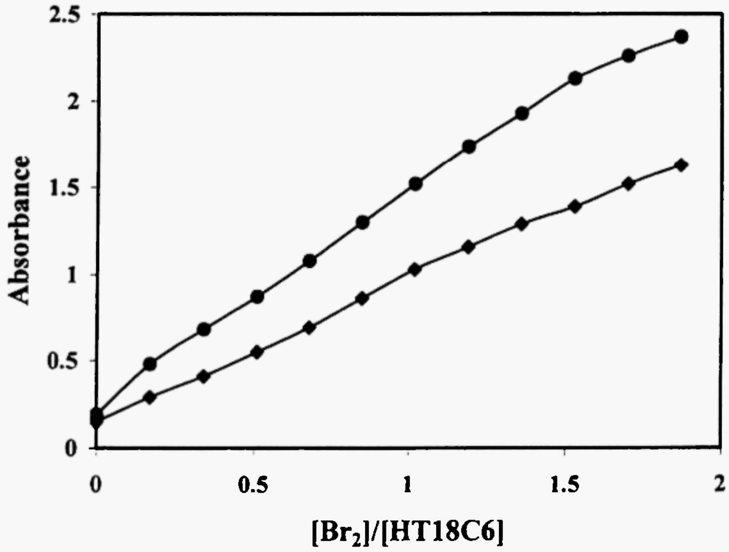


Fig. 7 Plots of absorbance vs. [Br_2]/[HT18C6] in CH_2Cl_2(•) and $CHCl_3$ (♦) solutions.

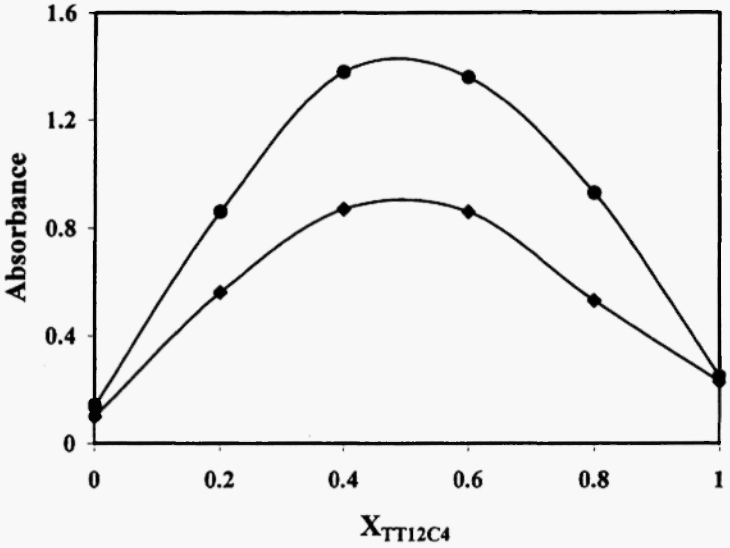


Fig. 8 Plots of absorbance vs. X_{TT12C4} in CH_2Cl_2(●) and $CHCl_3$ (◆) solutions.

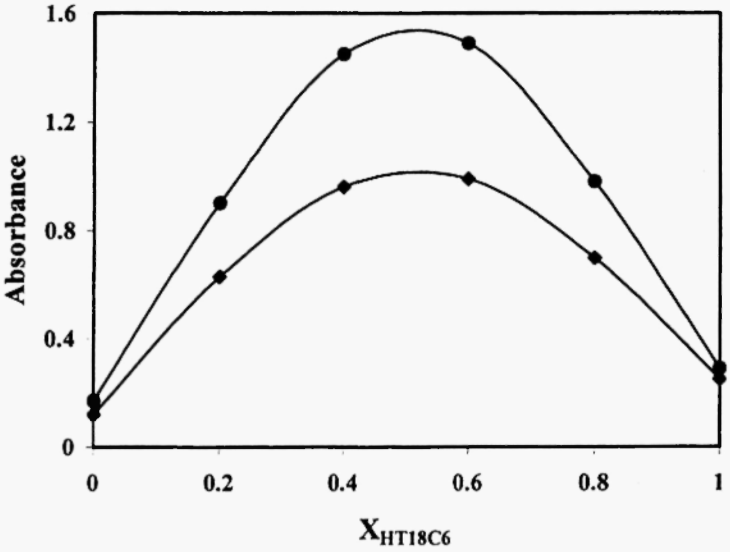


Fig. 9 Plots of absorbance vs. X_{HT18C6} in CH_2Cl_2(●) and $CHCl_3$ (◆) solutions.

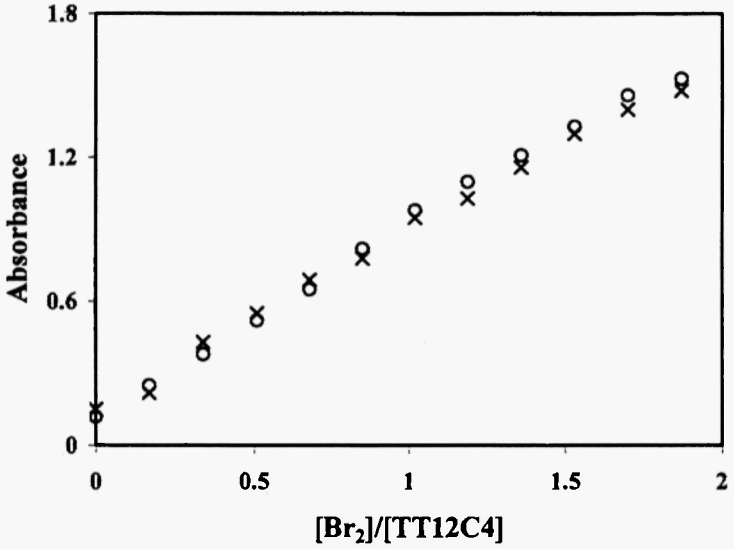


Fig. 10 Computer fitting of absorbance vs. $[Br_2]/[TT12C4]$ in $CHCl_3$ solutions.

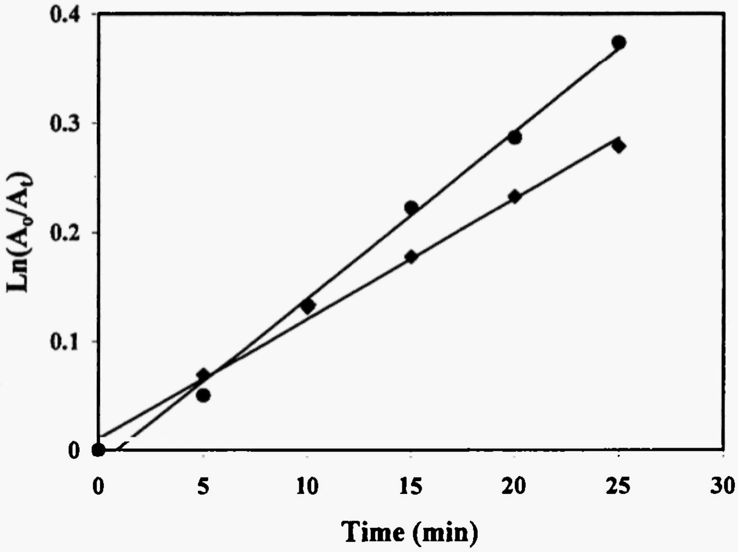


Fig. 11 Plots of $Ln(A_o/A_t)$ vs. time for 10^{-3} M of bromine and 10^{-3}M of TT12C4 in CH_2Cl_2(•) and $CHCl_3$ (♦) solutions.

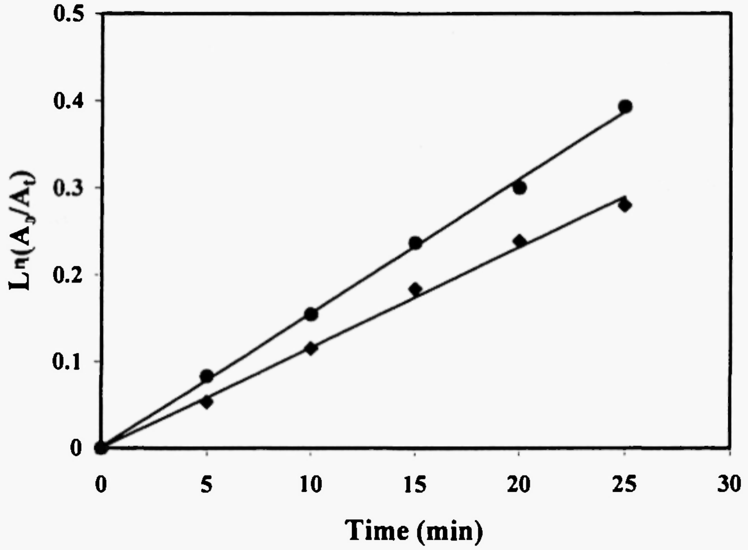


Fig. 12 Plots of Ln(A_0/A_t) vs. time for 10^{-3} M of bromine and 10^{-3} M of HT18C6 in CH_2Cl_2(●) and $CHCl_3$ (◆) solutions.

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