THERMODYNAMIC STUDY OF THE COMPLEXATION OF SOME THIACROWN ETHERS AND IODINE MONOBROMIDE IN CARBON TETRACHLORIDE SOLUTION

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Summary: Complexation of TT9C3, TT12C4 and HT18C6 as n-donor, with IBr as σ-acceptor has been studied at different temperatures in carbon tetrachloride solution. Spectrophotometric measurements have been carried out to obtain the stoichiometry, the equilibrium constants and thermodynamic parameters. The equilibrium constants of the resulting 1:1 complexes are calculated from the fitting of the absorbance mole ratio data in MATLAB software and found to vary in the order: HT18C6>TT9C3>TT12C4. The ΔH°, ΔS° and ΔG° values are obtained by the $\log K_f$ vs. 1/T plots. All of the complexes are enthalpy stabilized and entropy destabilized. The contribution of various factors on ΔH° and ΔS° are discussed. The plot of $T\Delta S^\circ$ vs. ΔH° is linear. The possible reasons for such linearity are discussed.

Key words: Spectrophotometry, Thiacrown ethers, Iodine monobromide, Thermodynamic, Carbon tetrachloride

Introduction

The tendency of ethers to form charge transfer complexes with halogens [1,2] and their ability to form oxonium ions with halogen acids [3,4] and to bind hydrogen halides by strong dipole-dipole interactions [5,6], as well as to act as effective solvating agents for cations [7, 8] are well established [9].

The macrocyclic polyethers, a class of compounds synthesized by Pedersen [10] was shown to bind cations much more powerfully than nonfunctional and linear polyfunctional ethers [11, 12]. A geometric fit between the size of cation and dimensions in the "cavity" in the macrocylclic molecule was shown to be, to a large extent, responsible for the stability of such complexes.

Recently, there has been considerable interest in the studies of charge- transfer complexes between macrocyclic crown ethers and a variety of acceptor molecules such as DDQ [13], TCNE [14], TCNQ [15], TNT [16] and specially iodine [17, 18]. The formed cavity by oxygen atoms in the macrocyclic polyethers [19] provides a very exciting feature to study their molecular encapsulation properties. Interest in such molecular complexes is strongly stimulated by their possible applications in areas like separation science, biomimetic receptors, catalysis of chemical reactions and conversion of chemical reactions into optical or electronic signals [20].

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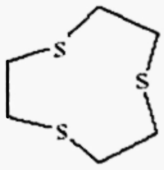
It has been clearly shown that the substitution of some of the oxygen atoms in the crown ether ring by sulphur atoms, alter their complexing ability towards metal ions [21]. The analytical applications of macrocyclic polythiacrown ethers in different areas have been reported [22-24]. However, to the best of our knowledge, there are only are limited number of published reports dealing with the molecular complexation of thiacrown ethers in solution [25, 26].

In recent years, we have been involved in the molecular complexes of crown ethers [27-30]. The present study deals with the complexation of iodine monobromide and some thiacrown ethers in carbon tetrachloride solution.

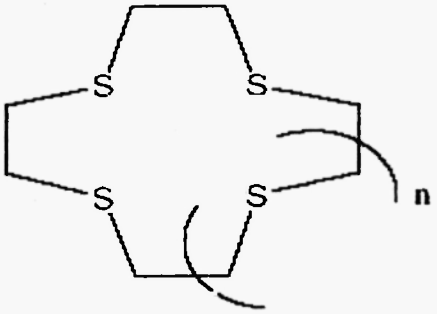
Experimental

Reagent grade HT18C6, TT9C3 and TT12C4 (all from Aldrich) were used as received. Reagent grade iodine monobromide (Ridel) and carbon tetrachloride (Merck) were of the highest purity available and used without any further purification.

The UV-Vis spectra were recorded on a UV-Vis Carry spectrophotometer model iso and the absorbance measurements were made with the same instrument at various temperatures (±0.05 °C).
In order to obtain UV-Vis spectra of macrocycles in the presence of varying concentrations of iodine, 3 mL of 10^{-3} M solution of macrocycle was transferred to a quartz cell and titrated with a concentrated solution of iodine monobromide. The same procedure was followed for the obtaining absorbance vs. mole ratio data at different temperatures. For obtaining the spectra of iodine monobromide in the presence of varying quantities of macrocycles, several solutions containing constant concentration of iodine monobromide (10^{-4} M) and different quantities of macrocycle prepared and the absorption spectra were recorded.



Trithia-9-crown–3 (TT9C3)



n=1, Tetrathia-12-crown-4 (TT12C4)
n=3, Hexathia-18-crown-6 (HT18

Results and discussion:

Absorption spectra of 10^{-3} M of TT9C3 in the presence of varying quantities of IBr at 25 °C are shown in Fig. 1. As it can be seen, upon addition of IBr two new bands are appeared at 290 and 490 nm, respectively. The 490 nm band in the spectra is corresponding to the free IBr. Meanwhile, the 290 nm band can be attributed to the formation of charge transfer complex between IBr as σ-acceptor and TT9C3 as n-donor [31]. Absorption spectra of TT12C4 and HT18C6 in the presence of varying concentrations of IBr (Figs. 2 and 3) are similar to TT9C3-IBr ones. So, in these cases also the formation of charge transfer complex is confirmed.

Absorption spectra of 10^{-3} M IBr in the presence of different quantities of TT9C3 are shown in Fig. 4. The observation of well defined isosbestic point at 430 nm is indicative of equilibrium reaction between TT9C3 and IBr [32]. Isosbestic point was also observed in other cases. However, the corresponding spectra are not shown.

In order to obtain the stoichiometry of the reactions the mole ratio method was followed [32]. The abserbance vs. [IBr]/Macrocycle] mole ratios are shown in Fig. 5. As seen, in all cases the existence of 1:1 stoichiometry is confirmed. Based on the spectral evidences (Figs 1-4) and mole ratio curves (Fig. 5), the interaction of IBr and macrocycle can be written as follows:

$$\text{Macrocycle} + \text{IBr} \rightleftarrows \text{Macrocycle. IBr} \qquad (1)$$

Marcocycle = TT9C3, TT12C4, HT18C6

The thermodynamic parameters of the reactions were evaluated from the measurement of the formation constants of the resulting complexes at different temperatures. The evaluations were followed from the absorbance-mole ratio data by using a non-linear least square curve-fitting program (curve-fitting toolbox in MATLAB). The program is based on the iteration adjustment of calculated absorbances to the observed values. The observed absorbance of complex is given by equation (2). The mass balance equation can be written as (3) and (4) and the formation constant of the complex as (5). Substitution of equations (3) and (4) into (5) and rearrangement yields equation (6).

$$A = \varepsilon[DA] \qquad (2)$$
$$C_D = [D] + [DA] \qquad (3)$$
$$C_A = [A] + [DA] \qquad (4)$$
$$K_f = [DA] / [D][A] \qquad (5)$$
$$K_f [DA]^2 - (C_AK_f + C_AK_f + 1)[DA] + K_fC_DC_A = 0 \qquad (6)$$

With use of an approximation value for K_f, the free DA concentrations, [DA], were calculated by solution of second order equation. Then, with using from of DA concentrations as X data and data of observed absorbances as Y data, the least square fit technique is used for fitting the data. The output of this fitting is the coefficients of line fit. The coefficient of X data is ε. The obtained coefficient was used for calculation data of calculated absorbances with using of parabolic fit. To find the least squares error, the sum of squares of the differences between the parabolic fit and the experimental data must be evaluated. Refinement of parameters (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 [33, 34].

The final computer fittings of absorbance vs. mole ratio data for different macrocycles at temperature 25 °C are shown in Figs. 6. The fair agreement between observed and calculated points confirms 1:1 stoichiometry in all temperatures. The obtained $\log K_f$ values as well as, the thermodynamic parameters resulted from $\log K_f$ vs. 1/T plots (Fig. 7) [35], are given in Table 1. As it can be seen: (i) the $\log K_f$ values in different temperatures vary in the order: HT18C6 > TT9C3 > TT12C4, (ii) all of the complexes are enthalpy stabilized and entropy destabilized, (iii) $|\Delta H^o|$ values vary in the order: HT18C6 > TT9C3 > TT12C4 and (iv) $|\Delta S^o|$ values vary in the order: HT18C6 > TT12C4 > TT9C3.

It is well known that the fitness of the cavity size of crown ethers and ionic diameter play an important role in the stability of ionic complexes of crown ethers [36]. Despite the introduction of IBr to thiacrown cavity causes the better overlapping conditions of sulphur and IBr orbitals. Neither Vander walls diameter of iodine [37], nor bromine [37] do not fit with no of macrocycles [38]. In fact the Vander Walls diameters of bromine and iodine are 3.70 and 3.96 A°, respectively [37]. Which are larger than the diameter of HT18C6 (2.6-3.4 A°) [38]. As, HT18C6 do have the largest cavity size among the series. The introduction of IBr into the cavity of other donors with lower cavity sizes is also discarded. On the other hand, the formation of charge transfer complex involves the proper orientation of sulphur orbitals toward IBr ones. This also needs the specific conformation of macrocycles. If the difference between the enthalpy of this conformation and the most stable conformation of free macrocycles to be low. The contribution of positive ΔH^o due to conformational changes would be low. Among the macrocycles, HT18C6 is most flexible one. Thus, the contribution of positive ΔH^o due to its conformational changes is low. Furthermore, the no. of donating atoms of this macrocycle is more than the others. Which causes the most negative ΔH^o of charge transfer. Thus, lowest positive of conformational changes and highest negative of charge transfer will result the most negative ΔH^o for the formation of HT18C6-IBr complex.

On the other hand, both the flexibility and the no. of donating atoms of TT9C3 is less than TT12C4. However, the ΔH^o of former is more negative than the latter one. This can be assigned to less conformational changes of TT9C3 than that of TT12C4 during complexation. Apparently, the conformation of free TT9C3 is suitable for complexation. So, the complexation of TT9C3 occurs with partial conformational changes. Which causes the less positive ΔH^o of conformational changes. The net effect is the more negative ΔH^o of TT9C3 than that of TT12C4.

The whole ΔS^o of complexation consist of three components (i) the difference between the conformational entropy of free and complexed macrocycle and (ii) the difference between the entropy due to no. of particles in reactants and product and (iii) the difference between the entropy of solvation of complex and desolvation of donor and acceptor.

In all of complexes two particles are converted to one paretic so, the contribution of first factor in whole ΔS^o is fixed and equal for all of complexes. On the other hand, through the complexation of HT18C6 the conformational freedom is highly lost. So, among the cycles macro the most negative ΔS^o due to this factor, belongs to HT18C6. TT12C4 and TT9C3 locate in the second and third order, respectively.

Dipole-induced dipole interactions between donor-solvent, acceptor-solvent and complex-solvent are the main factor that determines the degree of solvation of reactants and complex. So, the dipole moment of reactants in comparison with the complex determines the sign and the extent of third factor.

The plot of $T\Delta S^{o}$ vs. ΔH^{o} is shown in Fig. 8. There is a fairly good linear correlation between $T\Delta S^{o}$ and ΔH^{o} with the regression equation.

$$T\Delta S^{o}=\Delta S_{0} + m\Delta H^{o} \quad (7)$$

The existence of such a relation between $T\Delta S^{o}$ and ΔH^{o} frequently observed for a variety of metal-ligand [39-41] and charge transfer complexes [42, 43]. In the above equation $T\Delta S^{o}$ is the value of $T\Delta S_{0}$ in conditions that $\Delta H^{o}=0$. Equation (7) suggests that the entropic changes consist of two components. The first component $T\Delta S_{0}$ is independent of enthalpy change and the second ($m\Delta H^{o}$) is proportional to it. Based on the discussion on previous paragraph the whole ΔS^{o} was divided to three components. So, one of the constant or variable parts of $T\Delta S^{o}$ can be further divided to two components. Keeping in mind that the contribution of ΔS^{o} due to change in the no of particles is fixed and negative. The complete contribution of constant part to the recent factor would result in negative $T\Delta S^{o}$. However, it is positive. The positive $T\Delta S_{0}$ value of emphasizes that it is a combination of two constants. As the variability of ΔS^{o} due to conformational charges is certain. The constant part can be considered as a combination of ΔS^{o} of solvation–desolvation and ΔS^{o} of decreasing of the no. of particles during complexation. The positive sign of the sum of these two component and the negative sign of ΔS^{o} of change in no. of particles, indicate that the sign of salvation-desolvation ΔS^{o} is positive and its value is grater than, that of ΔS^{o} of the no. of particles.

Based on the results, it can be concluded that:
1) The interaction of all of the macrocycles proceeds through equilibrium pathway.
2) The stoichiometry of all of the complexes is 1:1
3) In none of macrocyles the interaction of IBr in the cavity do not occure.
4) The stability constants of all of complexes are high.
5) The formation of all of complexes is enthalpy stabilized and entropy destabilized.
6) The no. of donating atoms and the flexibility of the ligands play an important role in the ΔH^{o} values.
7) The ΔS^{o} of the process of desolvation of reactants and solvation of complex is positive and constant.

However, the ΔS^{o} of conformational changes during complexation is negative and variable.

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Table 1 Formation constants of different thiacrown–IBr complexes in carbon tetrachloride at various temperatures.

Macrocycle	**logK$_f$**			
	308 K	**298 K**	**288 K**	**278 K**
HT18C6	4.87±0.09	5.03±0.19	5.20±0.10	5.39±0.14
TT9C3	4.54±0.10	4.70±0.08	4.86±0.14	5.04±0.12
TT12C4	4.32±0.15	4.47±0.10	4.62±0.11	4.79±0.08

Table 2 Thermodynamic parameters for different thiacrown–IBr complexes in carbon tetrachloride solution.

Macrocycle	**ΔH° (KJ/mol)**	**ΔS° (J/mol K)**	**ΔG° (KJ/mol)**
HT18C6	-36.1±0.1	-25.0±1.0	-28.7±0.1
TT9C3	-33.3±0.1	-22.0±1.0	-26.8±0.1
TT12C4	-31.2±0.1	-19.0±1.0	-25.5±0.1

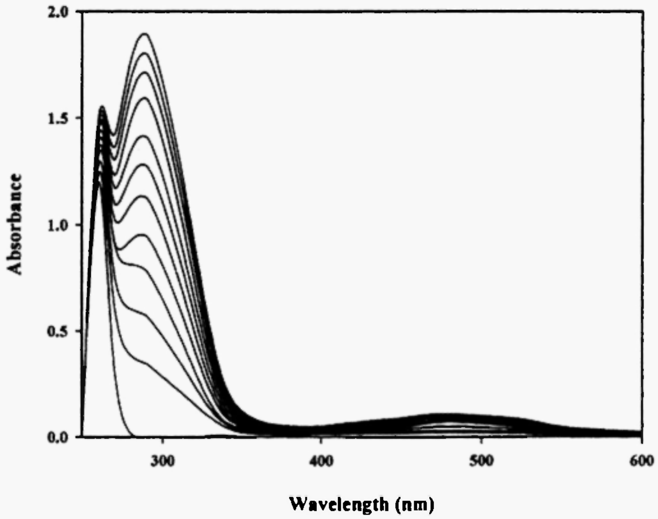

Fig. 1 Absorption spectra of 10^{-3} M of TT9C3 in carbon tetrachloride in the presence of varying quantities of IBr. The [IBr]/[TT9C3] mole ratios from bottom to top are: 0.00, 0.17, 0.34, 0.51, 0.68, 0.85, 1.02, 1.19, 1.36, 1.53, 1.70 and 1.87.

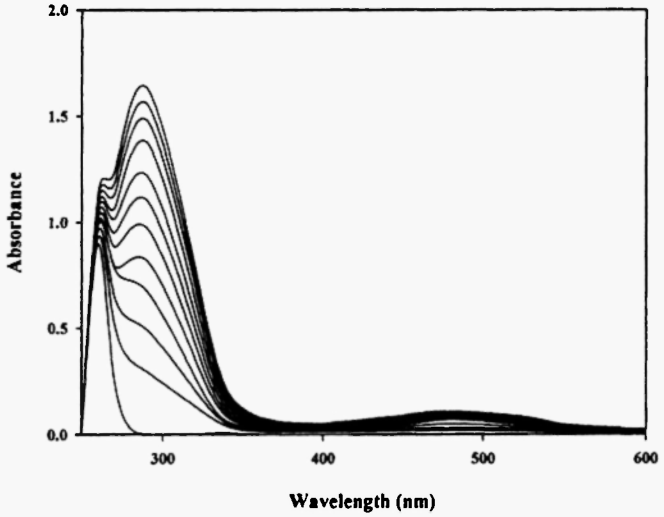

Fig. 2 Absorption spectra of 10^{-3} M solution of TT12C4 in carbon tetrachloride in the presence of varying quantities of IBr. The [IBr]/[TT12C4] mole ratios from bottom to top are: 0.00, 0.17, 0.34, 0.51, 0.68, 0.85, 1.02, 1.19, 1.36, 1.53, 1.70 and 1.87.

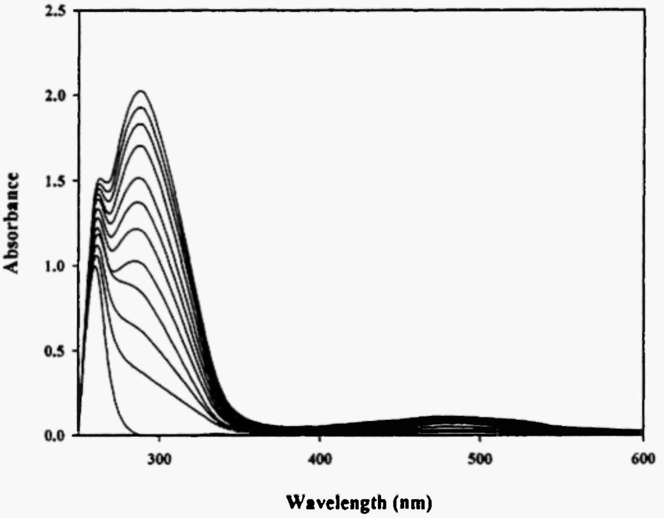

Fig. 3 Absorption spectra of 10^{-3} M solution of HT18C6 in carbon tetrachloride in the presence of varying quantities of IBr. The [IBr]/[HT18C6] mole ratios from bottom to top are: 0.00, 0.17, 0.34, 0.51, 0.68, 0.85, 1.02, 1.19, 1.36, 1.53, 1.70 and 1.87.

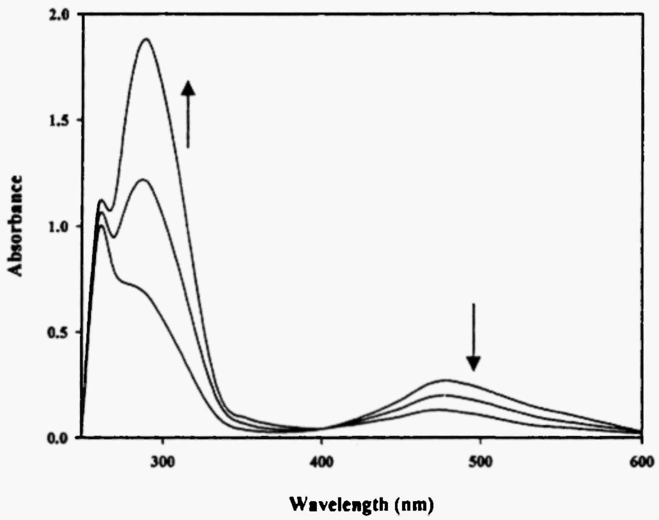

Fig. 4 Absorption spectra of 10^{-3} M solution of IBr in the presence of varying quantities of TT9C3. The [TT9C3]/[IBr] mole ratios from bottom to top are: 0.5, 1.0 and 1.5.

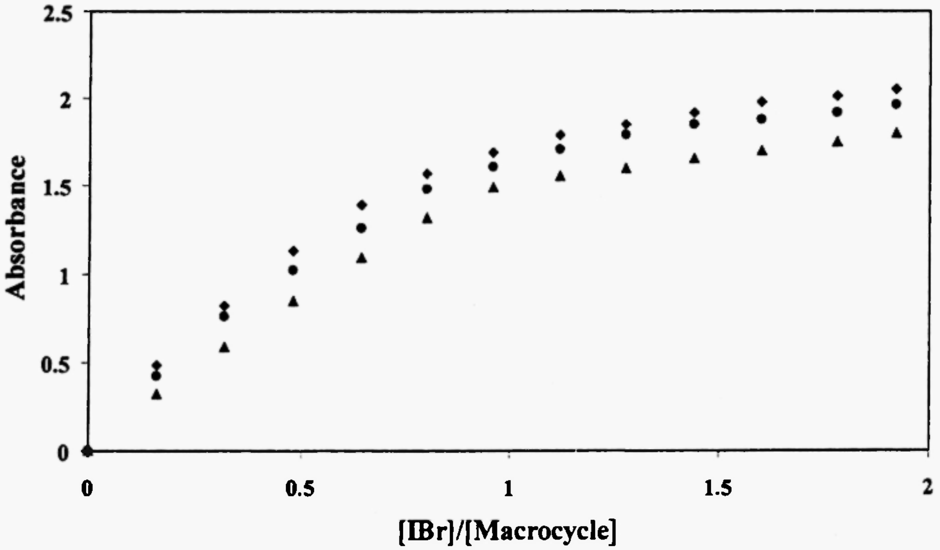

Fig. 5 Plots of absorbance vs. [IBr]/[Macrocycle] mole ratio at 290 nm and 25 °C, HT18C6 (◆), TT9C3 (•) and TT12C4 (▲).

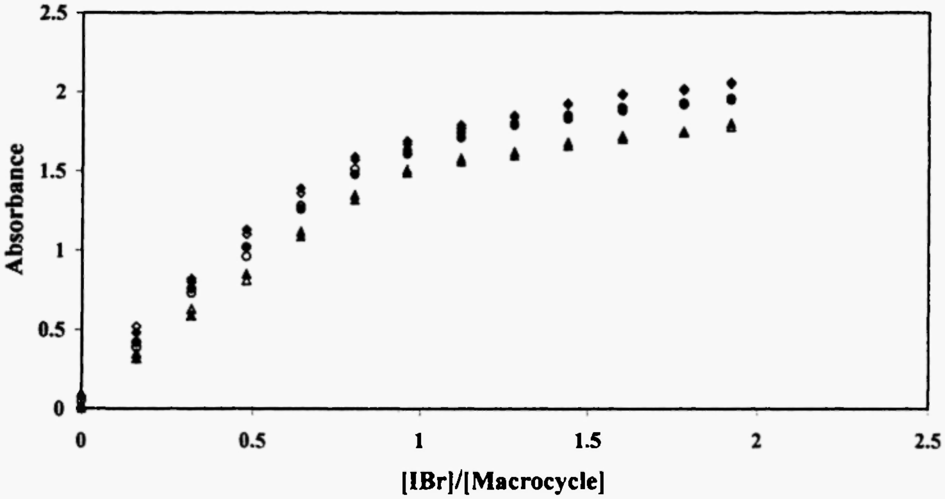

Fig. 6 Computer fitting of absorbance vs. [IBr]/[Macrocycle] mole ratio at 290 nm and 25 °C, HT18C6 (♦), TT9C3 (•) and TT12C4 (▲). The filled symbols and empty symbols are experimental and calculated points, respectively.

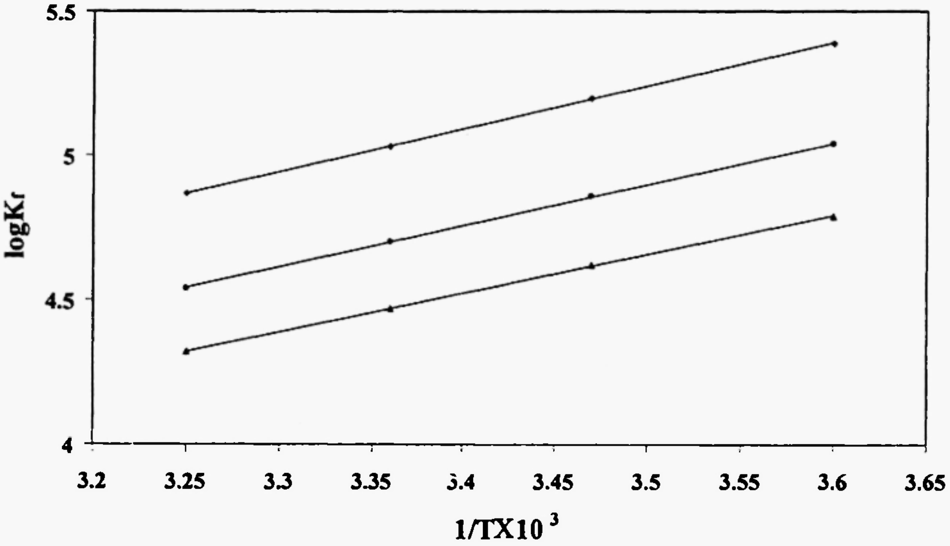

Fig. 7 Van't Hoff plots for iodine monobromide complexes with different thiacrown ethers in carbon tetrachloride solution, HT18C6 (♦), TT9C3 (•) and TT12C4 (▲).

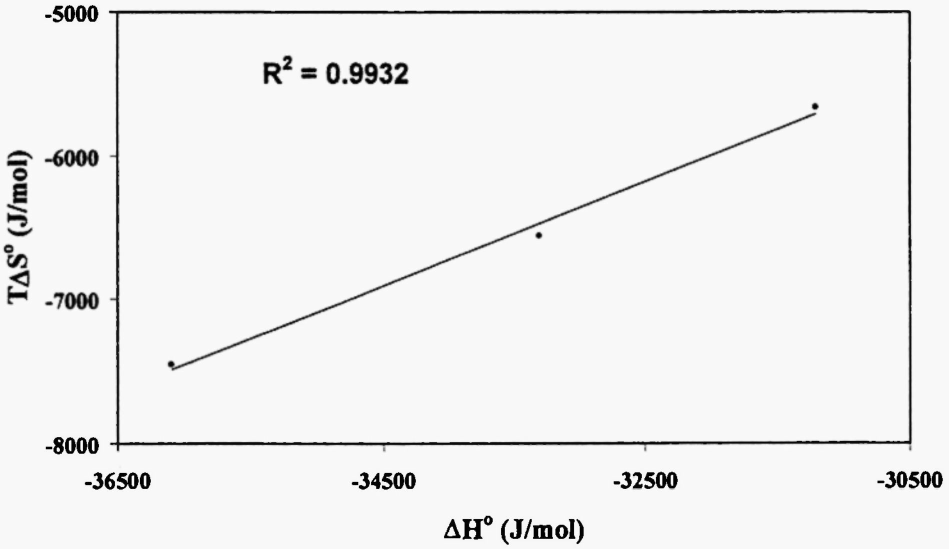

Fig. 10 Plots of TΔS° vs. ΔH° for different thiacrown-iodine monobromide complexes.