THERMODYNAMIC STUDY OF THE INTRACTION BETWEEN CRYPTAND 222 AND TETRACYANOETHYLENE IN CARBONTETRACHLORIDE SOLUTION

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Abstract- A spectrophotometric study concerning the interaction between 4, 7, 13, 16, 21, 24 -hexaoxa-1, 10 –diaza bicycle [8.8.8] hexacosane (cryptand C222) as n-donor and tetracyanoethylene (TCNE) as π-acceptor has been performed in carbontetrachloride solution at different temperatures. The results of job and mole ratio method are indicative of the formation of 1:1 charge transfer complex through an equilibrium reaction. The stability constants at different temperatures have been calculated from the computer fitting of absorbance-mole ratio data in MATLAB software. The ΔH^0 and ΔS^0 values are obtained by the Vant-Hoff method. The obtained data show that the complex is enthalpy stabilized and entropy destabilized. The solid complex was isolated and the effect of complexation on IR bands are discussed. The conductometric results indicate that none of the reactants and product do not alter the conductivity of solution and no free ion is formed through complexation.

Keyword: carbontetrachloride, C222, TCNE, Spectrophotometry, Charge transfer, Thermodynamic, Kinetic.

Introduction

In the past few decades there has been considerable interest in the studies of the charge transfer complexes between macrocyclic crown ethers and a variety of acceptor molecules such as DDQ [1-4], TCNQ [2], TCNE [2,3,5] and specially iodine [6-10]. Interest is such macrocyclic 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 in to optical or electronic signals [11].

Interestingly, it has been shown that the substitution of the oxygen atoms in crown ether ring by nitrogen results in a tremendous increase in stability of their complexes [4,5,8] over the ordinary crowns. From this point of view, the study of charge transfer complexes with at least two nitrogen atoms in their tridimensional cavities is of special interest. Following our previous works on molecular complexes of crown ethers [3,8,9,10,12-16], here we report the complex formation of cryptand 222 with tetracyanoethylene in carbontetrachloride solution.

Experimental

The macrocycle C222 and TCNE (Merck) were recrystallized from reagent grade n-hexane and dried over P_2O_5. Reagent grade carbontetrachloride (Merck) was used without any further purification.
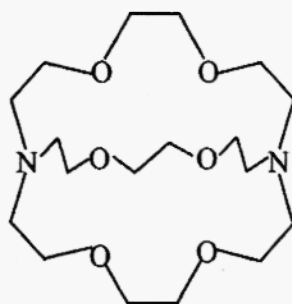
4, 7, 13, 16, 21, 24 - hexaoxa- 1, 10 – diaza bicycle [8.8.8] hexacosane
(Cryptand C222)
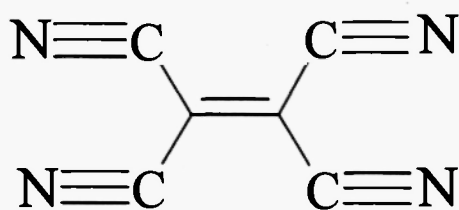
Tetracyanoethylene(TCNE)

All UV- Vis. spectra and absorbance measurement were made with a UV-Vis.-NIR spectrophotometer-Cary 500 at different temperatures. Conductance measurements were carried out with a conductivity meter 1800. IR spectra were recorded on a UV-Vis.-NIR spectrophotometer-Shimadzu 435 using KBr pellets.

Results and discussion

Absorption spectra of $1.0*10^{-4}$ M of C222 solution in the presence of varying concentrations of TCNE at 20 ^{0}C are shown in Fig. 1. Each spectrum was recorded one hour after preparing the solution. As it can be seen, upon addition of C222 to TCNE solution a new band is appeared in 350- 450 nm region. As none of reactants do not have any absorption in this region. The new band can be attributed to the formation of charge transfer complex between C222 as n-donor and TCNE as σ-acceptor[17]. The absorption spectra of C222 in the presence of varying concentrations of TCNE at 15, 10 and 5 ^{0}C are shown in Figs. 2-4, respectively. The comparison of recent spectra with those of 20^{0}C (Fig.1) indicate that upon increasing the temperature, the intensity of bands increases systematically. Such observation can be attributed to the alteration of stability constant, molar absorption coefficient or both of them. The stoichiometry of the complexes at different temperature was obtained by absorption vs. mole ratio [18] and Job methods [19]. The corresponding plots are shown in Figs.5 and 6. Both series of plots clearly confirm 1:1 stoichiometry. Moreover, in both cases upon increasment of temperature, the curvature of plots is decreased. Based on spectral, mole ratio and Job evidences, it can be concluded that through an equilibrium reaction between C222 and TCNE a 1:1 charge transfer complex if formed.

$$TCNE + C222 \leftrightarrows TCNE:C222 \tag{1}$$
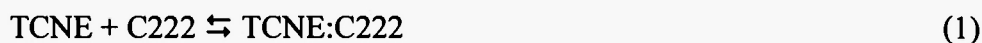
For the evaluation of the formation constants from absorbance-mole ratio data, a none-linear least squares curve fitting program (curve fitting toolbox in MATLAB) was used [20,21]. The program is based on the iteration adjustment of calculated absorbances to the observed values.

The observed absorbance of complex at it's 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) and rearrangement yield (6).

$$Abs. = \varepsilon \, [DA] \tag{2}$$

$$C_D = [D] + [DA] \tag{3}$$

$$C_A = [A] + [DA] \tag{4}$$

$$K_f = [DA]/[D][A] \tag{5}$$

$$K_f \, [DA]^2 - (C_A \, K_f + C_D \, K_f + 1) \, [DA] + K_f \, C_D \, C_A = 0 \tag{6}$$

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 use for fitting the data. The out put of this fitting is the coefficient of line fit. The coefficient of x values is ε (molar absorptivity coefficient). The obtained coefficient were used for calculation data of absorbance with using of parabolic fit. To find the least squares error, the sum of squares of differences between the parabolic fit and the actually 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.

The corresponding curve fitting are shown in Fig. 7. The good agreement between the experimental and calculated data confirms the accuracy of the results. The final log K_f and ε values obtained by MATLAB are given in Table 1. Beside this data the log K_f values which have been obtained by Job plots (sample calculation method at 25^0C is shown in Fig.8), are also given. The data in Table 1. show a good agreement between the MATLAB out put and those which have been obtained by Job plots. Otherwise the systematic increase of log K_f upon decreasing of temperature is confirmed. Finally, the rising of ε values at higher temperatures prove that the increase of the band intensities upon temperature increasment (Fig.1-4), can not be attributed to the formation constants and merely relate to ε alteration. The thermodynamic parameters were obtained by the plot of log K_f vs. 1/T (Fig. 8) [22]. The obtained values are: $\Delta H^0 = -28.25$ kJ/mol and $\Delta S^0 = -31.41$ J/ mol. ^0K. The negative value of ΔS^0 is not unexpected, Because two particles are converted to one particle. As, there is no special solvation effect. The play don't have any important role in the complexation process.

A conductometeric study was performed and it was found that the formation of charge transfer complex is nonionic[24].

The IR spectra of C222, TCNE and the resulting 1:1 complex are compared in Fig. 9. As it can be seen, upon complexation, (i) the intensity of band are reduced, (ii) the CH stretching bands of C222 at ~3000 cm^{-1} had not shifted considerably, (iii) the CN stretching bands of TCNE at 2280 cm^{-1} has been shifted to 1559 cm^{-1}. (iv)the CH2 bending of C222 at 1419 cm^{-1} has been shifted to 1556 cm^{-1},(v)the C-N stretching of C222 at 1266 cm^{-1} has been shifted to 1315 cm^{-1}, however the corresponding C-O band at 1233 show a little shift to higher frequencies, and finally the C-C band of TCNE at 1161 cm^{-1} has been shifted to 1201 cm^{-1}.

Simillar effects have been observed for some other charge transfer complexes [25,26] .The first effect can be attributed to the increasement of symmetry upon complexation. The second observation show that complexation has not affected the C-H stretching. The third effect can be assigned to creation of negative charge on the carbons of C=C band of TCNE upon complexation . Which results in the increasement of the role of the resonance structure of (B). As in structure of (B) the CN band to have some double band character, the corresponding stretching band appear at lower frequencies.

A   **B**
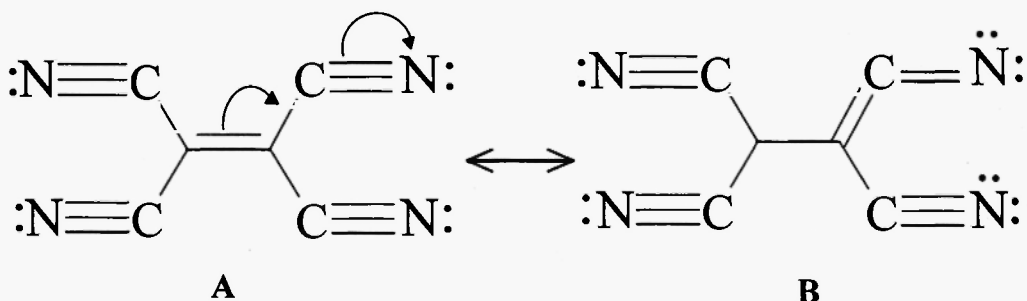
The fourth effect can be related to the diminishing the bending of methylene group of C222 upon complexation. The fifth observation results from the direct involvement of nitrogen atoms and unparticipation of oxygen atoms on complexation. Finally, similar to third one the last effect results from the increasement of the role of resonance structure of (B) which causes some double band character for single C-CN band of TCNE.
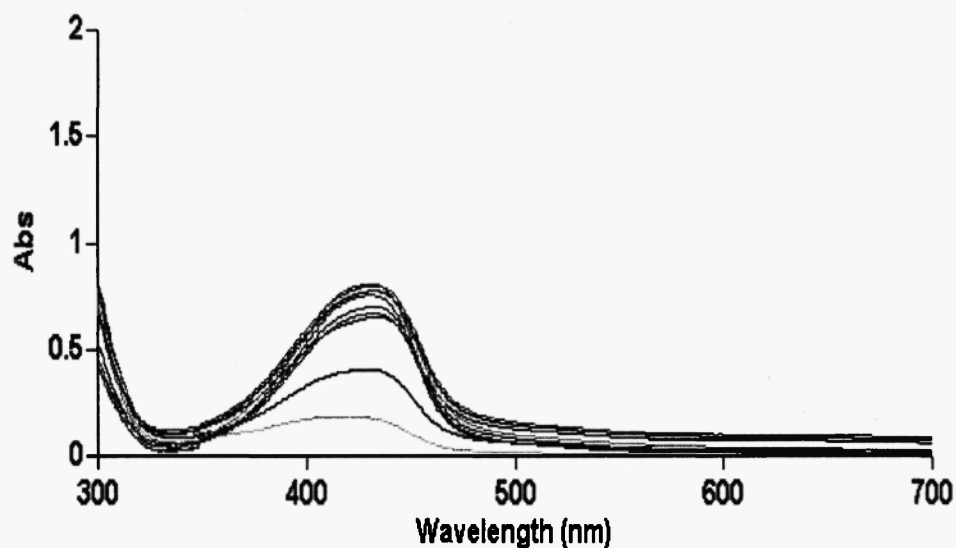
Fig.1 Absorption spectra of 1.0×10^{-4} M C222 in the presence of varying concentration of TCNE at 20 ^{0}C. The ratio of TCNE to C222 from bottom to top are: 0.33, 0.50, 0.67, 0.80, 1.00, 1.33, 1.50, 1.67, 2.00, 2.33, 2.50, 2.67.
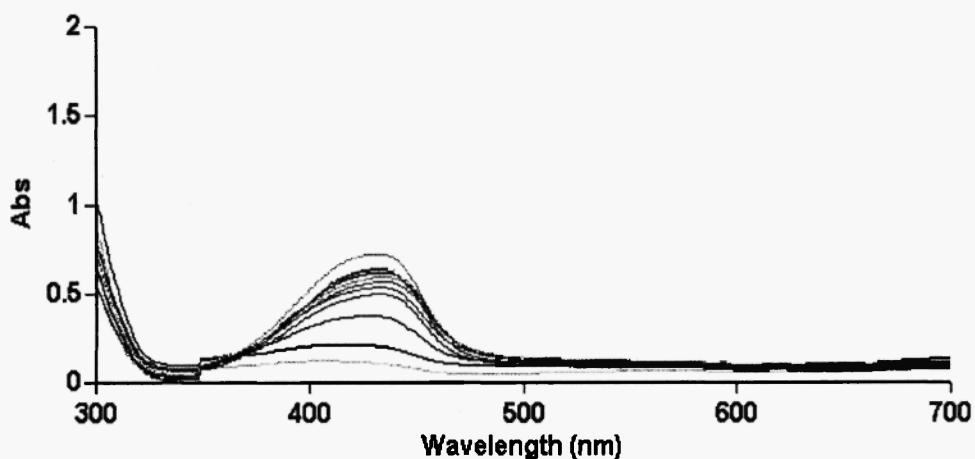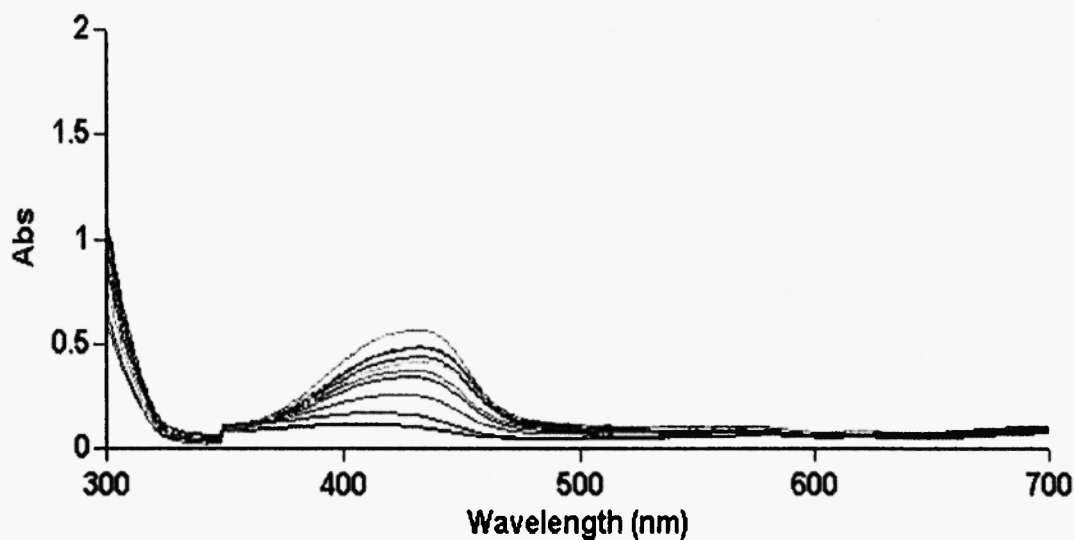

Fig.2 Absorption spectra of 1.0×10^{-4} M C222 in the presence of varying concentration of TCNE at 15 ^{0}C. The ratio of TCNE to C222 from bottom to top are: 0.33, 0.50, 0.67, 0.80, 1.00, 1.33, 1.50, 1.67, 2.00, 2.33, 2.50, 2.67.

Fig.3 Absorption spectra of 1.0×10^{-4} M C222 in the presence of varying concentration of TCNE at 10 ^{0}C. The ratio of TCNE to C222 from bottom to top are: 0.33, 0.50, 0.67, 0.80, 1.00, 1.33, 1.50, 1.67, 2.00, 2.33, 2.50, 2.67.
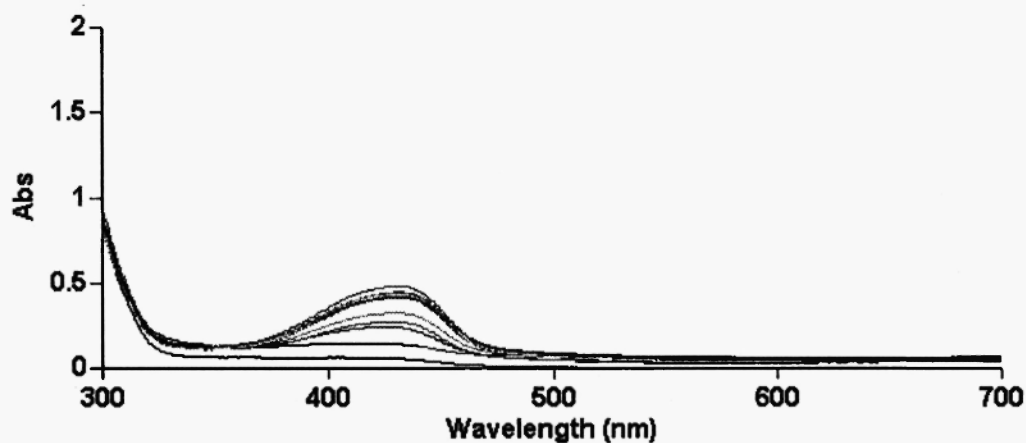

Fig.4 Absorption spectra of 1.0×10^{-4} M C222 in the presence of varying concentration of TCNE at 5 ^{0}C. The ratio of TCNE to C222 from bottom to top are: 0.33, 0.50, 0.67, 0.80, 1.00, 1.33, 1.50, 1.67, 2.00, 2.33, 2.50, 2.67.
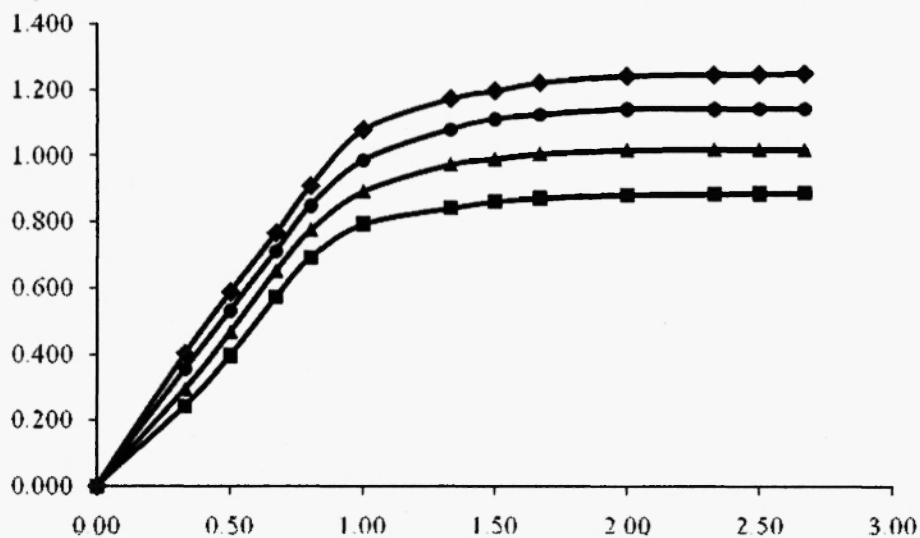
Fig.5 Absorbance vs. mole ratio plots for 1.0×10^{-4} M C222 at different temperatures. (■) 5 ^{0}C, (▲) 10 ^{0}C, (●) 15^{0}C and (♦) 20 ^{0}C.
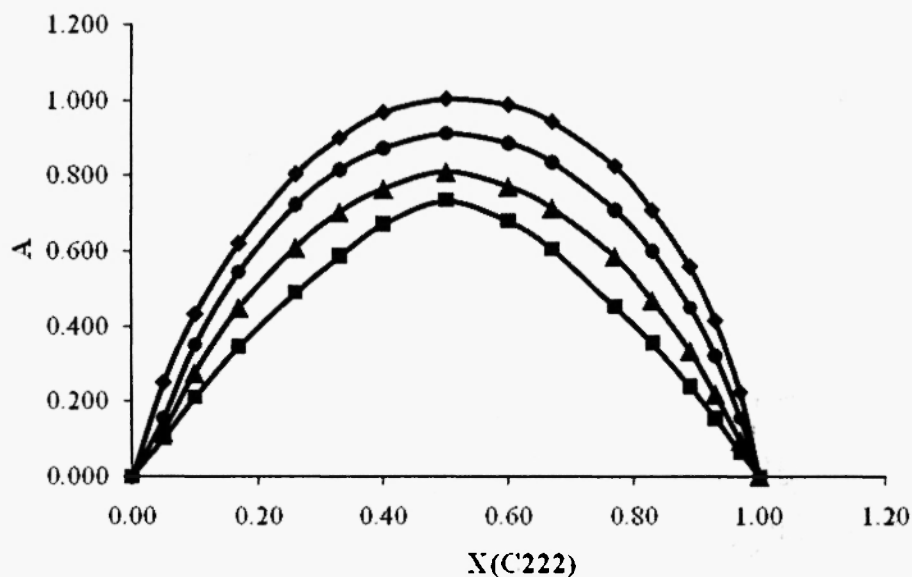

X(C222)

Fig.6 Job plots at different temperatures. The concentration of stock solutions and the final volume of each solution are 1.0×10^{-3} M and 1000μl, respectively. (■) 5 ^{0}C, (▲) 10 ^{0}C, (●) 15^{0}C and (♦) 20 ^{0}C.
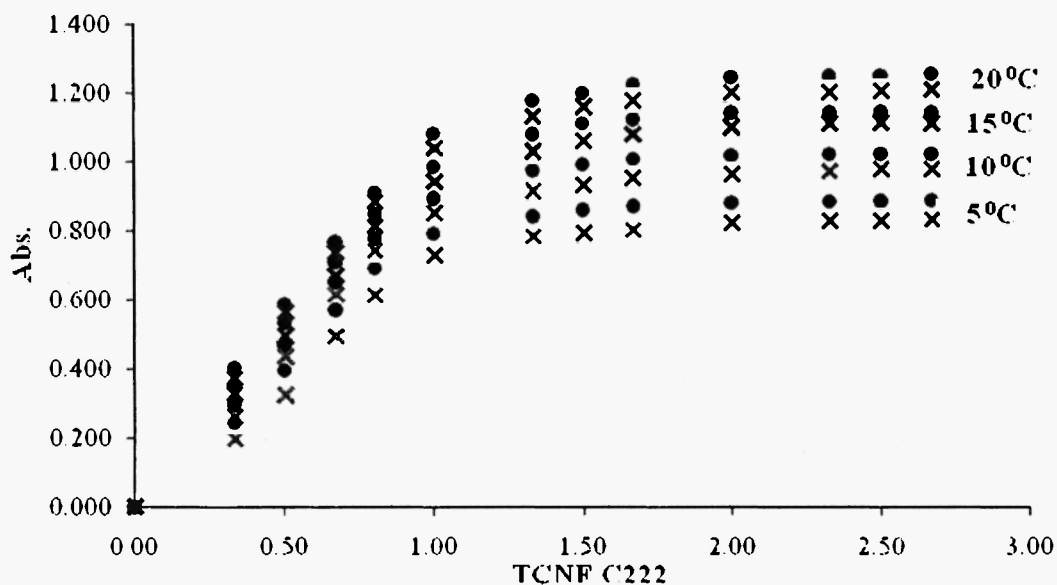
Fig.7 Computer fitting of absorbance vs. mole ratio data at different temperatures; (×) experimental points and (○) calculated points.

Table 1. Finall log K_f and ε values at different temperatures.

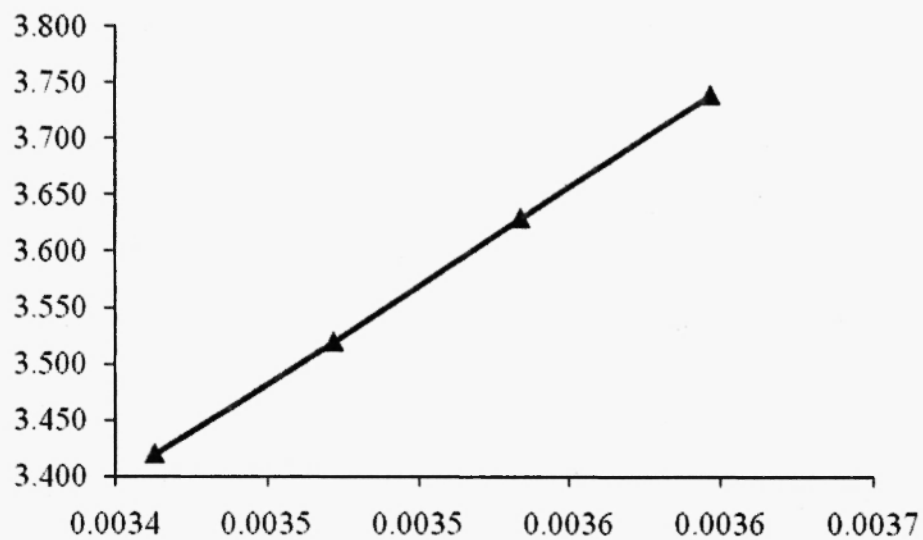| T	278	283	288	293
log K_f by MATLAB	3.69±0.03	3.60±0.02	3.51±0.02	3.42±0.01
log K_f by Job's Method	3.74±0.01	3.63±0.01	3.52±0.01	3.44±0.01
ε	1763±0.02	2327±0.02	2905±0.01	3485±0.01

$\Delta H^0 = -28.25$ kJ/mol $\Delta S^0 = -31.41$ J/mol.K

Fig.8 The plot of log K_f vs. 1/T.

$\Delta H^0 = -28.25$ kJ/mol, $\Delta S^0 = -31.41$ J/mol.K
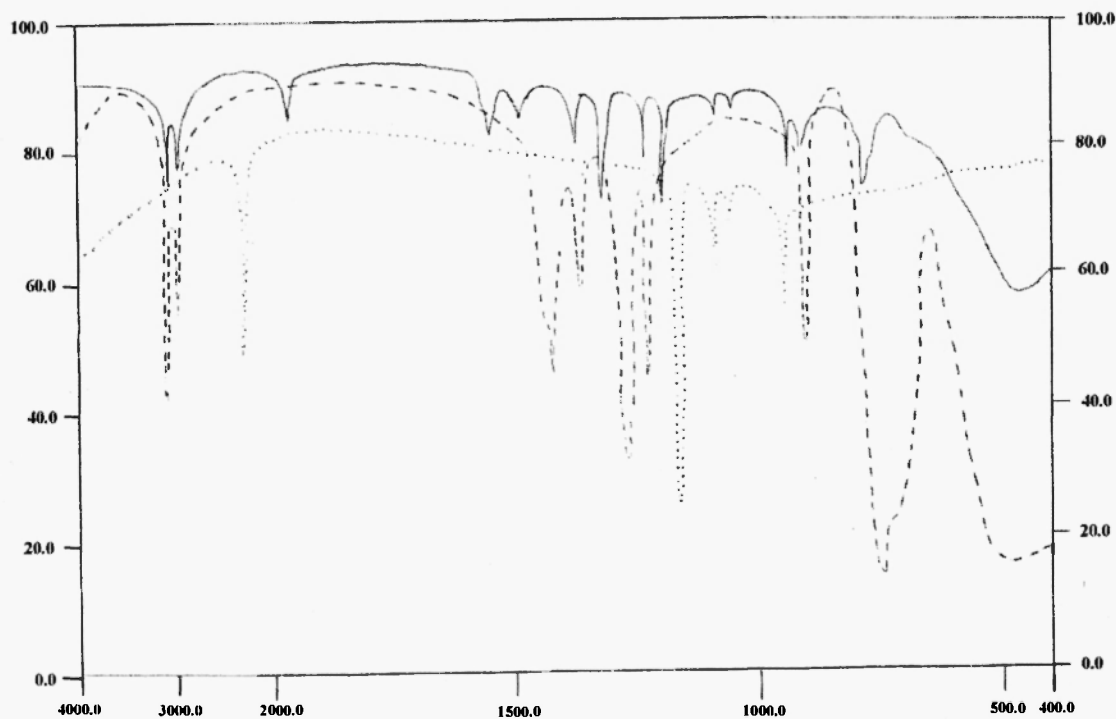

Fig.11- IR spectra of TCNE (dot lines), C222 (dash lines) and the 1:1 complex (solid lines).

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