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By Abolfazl Semnani, Ali Reza Firooz, Leila Kashefi Kheyrabadi, Hamid Shakoori Langeroodi , Safieh Heidarizadeh Rizi

University of Isfahan, Isfahan, 81746-73441, I.R. Iran

Abstract - A spectrophotometric study concerning the interaction between cryptand 222 as n-donor and TCNE as π - acceptor has been performed in di and tri chloromethane solutions at temperatures 5, 10, 15, and 20°c. The results of continuous variation and mole ratio methods indicate the formation of 1:1 complexes in both solvents and at all temperatures. The stability constants and the molar absorption coefficients at different temperatures have been calculated from the computer fitting of absorbance- mole ratio data in **MATLAB** soft ware. The results indicate that Kf values in $\mathbf{CHCl_3}$ are more than the corresponding amounts in $\mathbf{CH_2Cl_2}$. In the case of **€**, the reverse trend is observed. The $\Delta H°$ and $\Delta S°$ values were obtained by Vant Hoff method. The obtained data show that the enthalpy of complex formation in two solvents is favorable. While entropy is favorable in the case of $\mathbf{CHCl_3}$ and unfavorable in the case, of $\mathbf{CH_2Cl_2}$. The possible reasons for such observation are discussed. The kinetic results confirm an overall second order reaction which is first order with regard to each reactant. The formation of free ions is rejected by the conductometric measurments.

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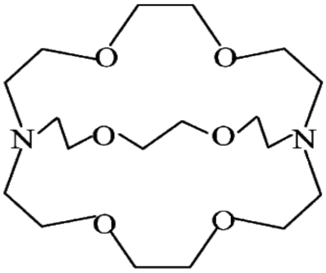
I. INTRODUCTION

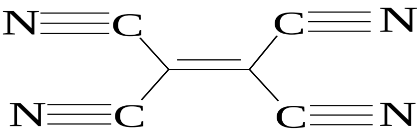
Since the first synthesis of crown ethers [1] and cryptands [2], there has been an intensive amount of research work on the thermodynamic and kinetics of complexation of these ligands with various cations in a wide variety of solvent systems [3]. Moreover, the molecular complexes of crowns and cryptands have been followed [4]. Interest in molecular complexes is strongly stimulated by their possible applications in different areas such as separation processes, biomimetric receptors, catalytic reactions and conversion of chemical energy to optical or electronic signals. In continue of our interest to molecular complexes of crowns and cryptands [5-10], here we report the results of complexation of cryptand 222 with TCNE in di and trichlolromethane solutions.

II. EXPERIMENTAL

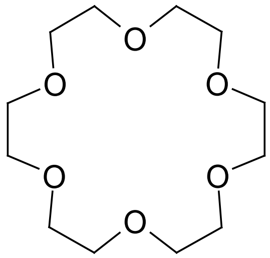
The macrocycle C222 and TCNE (both from Merck) were recrystallized from reagent gradre n-hexane and dried over P2O5. Reagent grades of di and trichlorometahne (both from Merck) were used without any further purification.



Cryptand 222 (C222)



Tetracyanoethylene (TCNE)



18-Crown-6

All UV-Vis spectra and absorbance measurements were made with a UV-Vis-NIR spectrophotometer Cary 500 at different temperatures.

Author [α] [¥] : Department of Chemistry, Faculty of Science, University of Isfahan, Isfahan, 81746-73441, I.R. Iran.
Author [Ω] [β] : Department of Chemistry, Faculty of Science, University of Shahrekord, Shahrekord, 115, I.R. Iran.
Author [ψ] : Petrokimia Sepahan Company, Mobarekeh Industrial City, Isfahan, Iran.

Conductance measurements were carried out with a conductivity meter 180 from Orion research Company.

III. RESULTS AND DISCUSSION

Absorption spectra of 1.0× 10-4 M solution of C222 in trichloromethane in the precence of varying concenteations of TCNE are shown in Fig. 1. Because of similarity, the corresponding spectra due to dichloromethane are not shown. Each spectrum was recorded 20 minutes after preparing the fresh solution. As it can be seen upon addition of C222 to the solution of TCNE, a new band is appeared in 350-450 nm region. As, none of the reactants, do not have any absorption in this spectral region. The new band can be attributed to the formation of charge transfer complex between C222 as n-donor and TCNE as π - acceptor [11].

In order to determine the effective site of complexation, the spectrum of 1:1 mixture of 18C6 (i.e. a compound without nitrogen atom) and TCNE was recorded. As, new band was not observed, it can be concluded that the oxygen atoms of C222 do not play an important role and the complexation mainly occur through nitrogen atoms.

The needed time for reaction completeness was determined by monitoring the absorbance of 1:1 mixture of 1.0×10-4 M solution of C222 and TCNE at 400 nm and at different temperatures (Fig. 2). As it can be seen, after 15 minutes, reaction will be terminated. Therefore, in the next experiments, absorbances were measures 20 minutes after mixinof reagents.

The stoichiometry of the complexes at different temperatures was obtained by the absorbance vs. mole ratio [12] and Job methods [13]. Sample plots are shown in Figs. 3 and 4, respectively. Both series of plots clearly confirm 1:1 stoichiometry. Moreover, in both cases upon temperature rising, the curvature of plots is decreased.

Based on spectral, mole ratio and Job evidences it can be concluded that through the reaction between C222 and TCNE, 1:1 charge transfer complex is formed.

$$\text{TCNE} + \text{C222} \leftrightarrows \text{TCNE: C222} \tag{1}$$

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 [14,15]. The program is based on the iteration adjustment of calculated absorbances to the observed values.

The observed absorbance of complex at its λmax 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 (3) and (4) in (5) and rearrangement yield (6).

$$\text{Abs.} = \epsilon b[DA] \tag{2}$$

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

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

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

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

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 used for fitting the data. The output of this fitting is the coefficient of line fit. The coefficient of x values is ϵ (molar absorption coefficient). The obtained coefficient were used for calculation of 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.

Sample curve fittings are shown in Fig. 5. The good agreement between the experimental and calculated data confirm the accuracy of the results. The final logKf and ϵ values obtained by MATLAB are given in Table 1. The data indicate that at all temperatures logKf values due to trichloromethane are higher than the corresponding values in dichloromethane. In the case of ϵ, the reverse trend is observed. Greater $\log K_f$ in trichloromethane means that in this media, the contribution of solvent in entropy, enthalpy or both of them is more favorable than dichloromethane. On the other hand, despite both TCNE and C222 are nonpolar. Their resulting complex is polar and will show diplole-diploe interactions with polar species. Clearly, such interactions will be higher with more polar species. So, it is anticipated that dicholoromethane with dipole moment of 1.5 [16], do have more solute–solvent interactions (with polar charge transfer complex) than that of trichloromethane with dipole moment of 1.15 [16]. Greater dipole-dipole interactions cause that in CH_2Cl_2 orientation of complex particles to be more than of $CHCl_3$. This results in higher absorption cross section [17]. The net effect is the enhancement of ϵ. Therefore, the observation of higher ϵ in CH_2Cl_2 is not unexpected.

The thermodynamic parameters were obtained by the plot of $\log K_f$ vs. $1/T$ (sample plot is shown in Fig. 6) [18]. The obtained values for $\Delta H°$ are -26.3 kJ/mol and -25.4 kJ/mol in di and trichloromethane, respectively. Also, the $\Delta S°$ values were obtained as -16.3 J/mol.°K in dichloromethane and +25.13 J/mol.°K in trichloromethane.

It is well known that the final stability of complex depends on the sum of entropy and enthalpy changes through the complexation process [18]. On the other hand, the salvation, affects both $\Delta S°$ and $\Delta H°$ values. The effect on $\Delta S°$, relates to positive entropy changes due to desolvation of reactants and negative entropy changes due to solvation of complex. The effect on $\Delta H°$, relates to enthalpy changes during desolvation of reactants and solvation of complex.

The enhanced enthalpy changes in both solvents indicate that the amount of realized energy through complex formation and complex solvation is higher than consumed energy for desolvation of reactants. In addition, positive $\Delta S°$ in dichloromethane indicates that absolute entropy increase through desolvation of reactants is more than absolute entropy decrease through complex formation and complex solvation. Negative $\Delta S°$ in trichloromethane proves that entropy changes through desolvation of reactants or solvation of complex in recent solvent differs from corresponding values of dichloromethane.

The existence of nitrogen atoms on C222 and TCNE beside the location of three electron-withdrawing groups on carbon atom of trichloromethane, enhances the hydrogen bond formation between solvent and reactants. These bonds are broken through complex formation and some solvent molecules are realized in solvent. The net result is the positive $\Delta S°$. In the case of dichloromethane, the hydrogen bonds are considerably weaker. So, positive effect (through solvent realization) on overall $\Delta S°$ is considerably less than trichloromethane, which causes the observation of overall negative $\Delta S°$ in this solvent.

With the aim of determination of reaction order relative to each of reactants, the absorbance of the various solutions with different TCNE/C222 mole ratios were measured. The measurements were made two minutes after mixing the reactatns. Sample data due to trichloromethane are given in Tables 2 and 3, respectively. As it can be seen, at all temperatures and in both cases, the variation of absorbance is proportional to the variation of TCNE/C222 mole ratio or vice versa. Similar trend was observed in dichloroemethane. Based on the recent data it can be concluded that in both solvents a second order reaction in which the order of TCNE and C222 are 1 is followed.

The conductances as a function of C222/TCNE or TCNE/C222 in both solvents were measured. Considerable change was not observed. So it can be concluded that the adducts of TCNE and C222 in both solvents are nonionic.

IV. CONCLUSIONS

Based on the obtained results it can be concluded that:

1. In both solvents 1:1 complexes are formed.
2. The stability of complexes in $CHCl_3$ are higher than CH_2Cl_2.
3. The ϵ of complexes in CH_2Cl_2 are greater than $CHCl_3$.
4. In both solvents, the $\Delta H°$ of complex formation are negative.
5. Because of hydrogen bonding between the solvent and reactants, the $\Delta S°$ $CHCl_3$ is positive.
6. At all temperatures, the reaction order relative to both of reactants is 1:1
7. The resulting adducts are nonionic.

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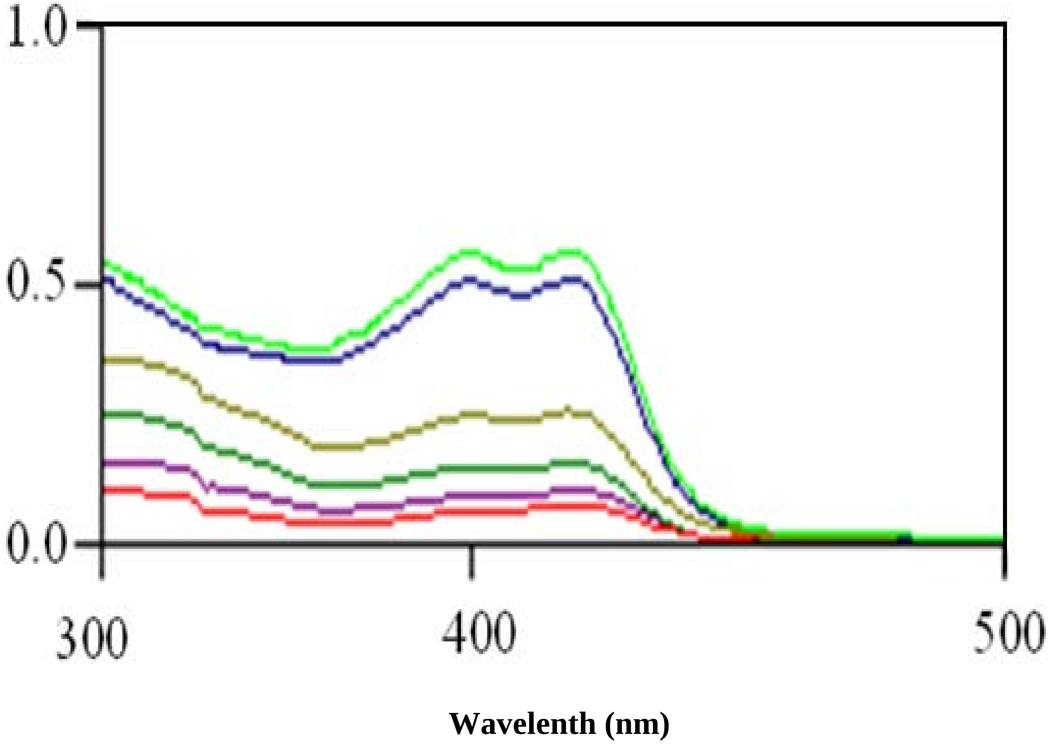

Fig. 1 : Absorption spectra of 1.0×10-4 M C222 in the presence of varying concentration of TCNE at 20 0C. The ratio of TCNE to C222 from bottom to top are: 0.15, 0.25, 0.50, 1.00, 1.50, 2.5.

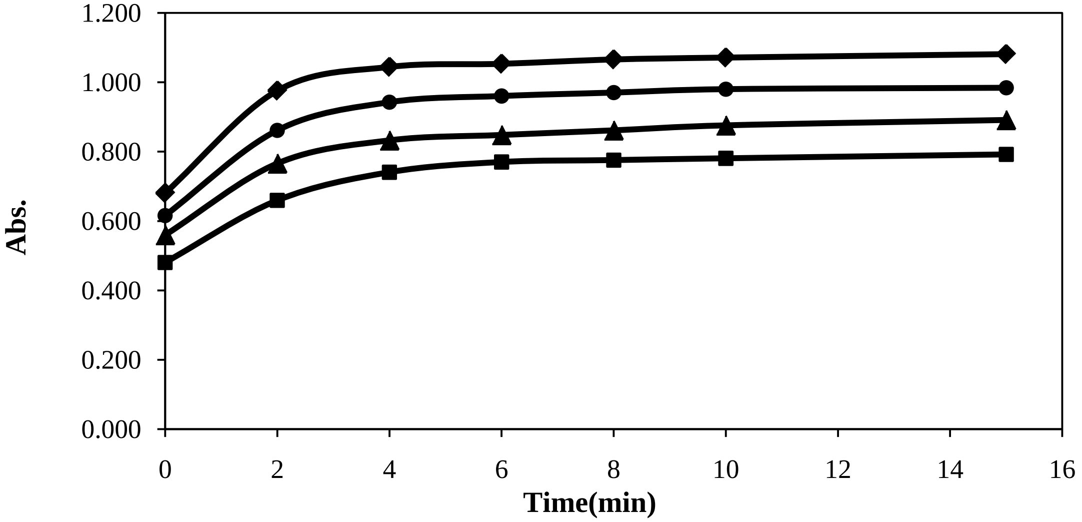

Fig. 2 : Plots of absorbance vs. time for 1.0× 10-4 M C222 in trichloromethane in different temperatures. From bottom to top: 5, 10, 15, and 20°c.

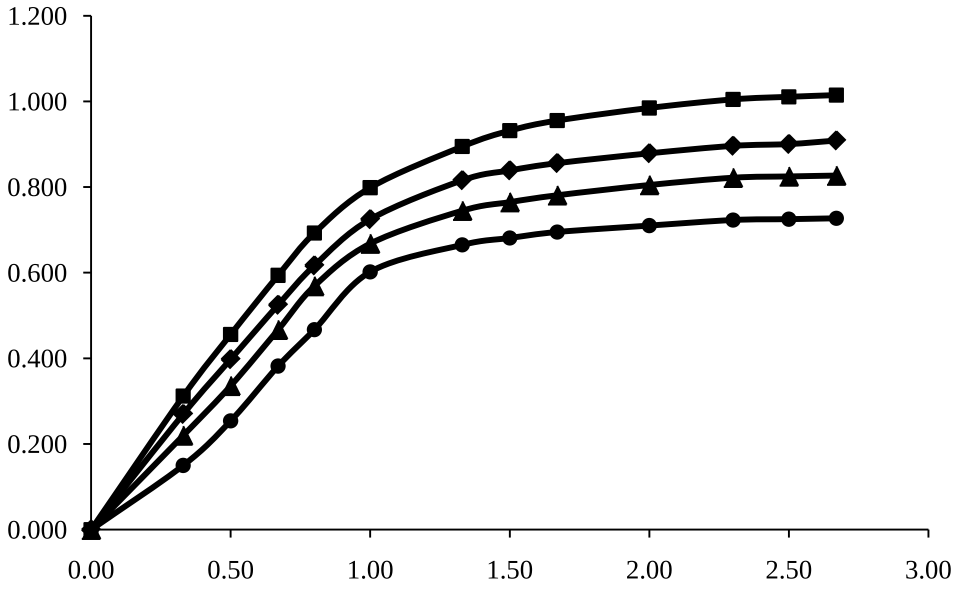

Fig.3 : Absorbance vs. mole ratio plots for 2.0×10-4 M C222 in dichloromethane solution at different temperatures. (■) 5 0C, (▲) 10 0C, (●) 150C and (♦) 20 0C.

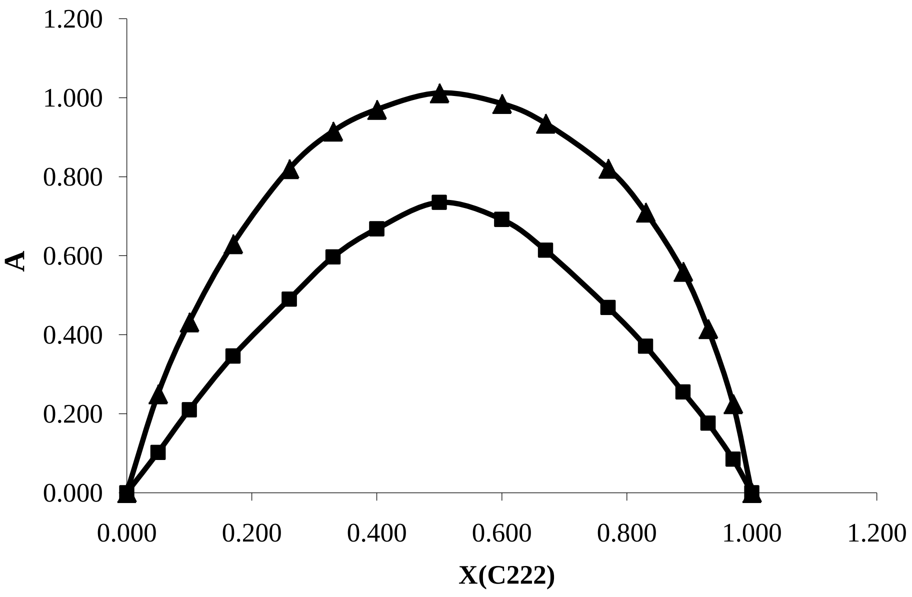

Fig.4 : Job plots at different temperatures in dichloromethane. The concentration of stock solutions and the final volume of each solution are 2.5×10-4 M and 3ml, respectively. (■) 5 0C, and (●) 20 0C.

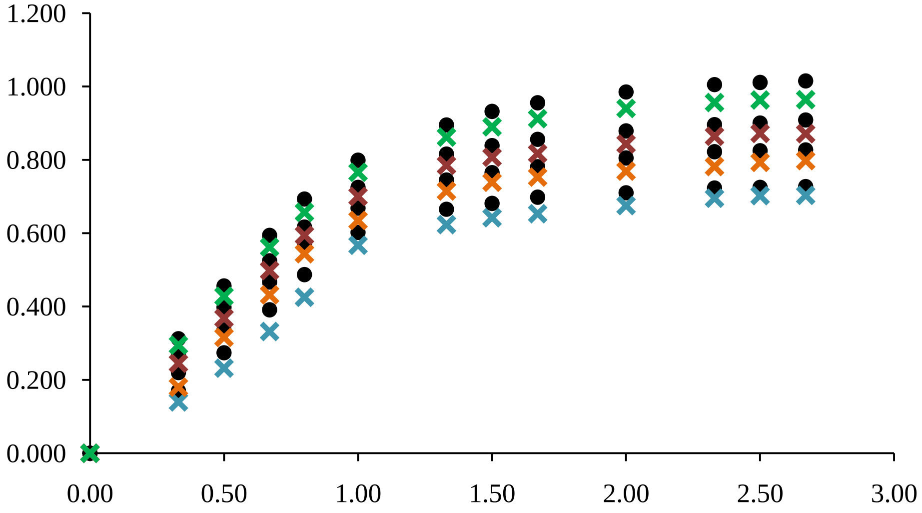

Fig.5 : Computer fitting of absorbance vs. mole ratio data indichloromethane at different temperatures; (●) experimental points and (×) calculated points.

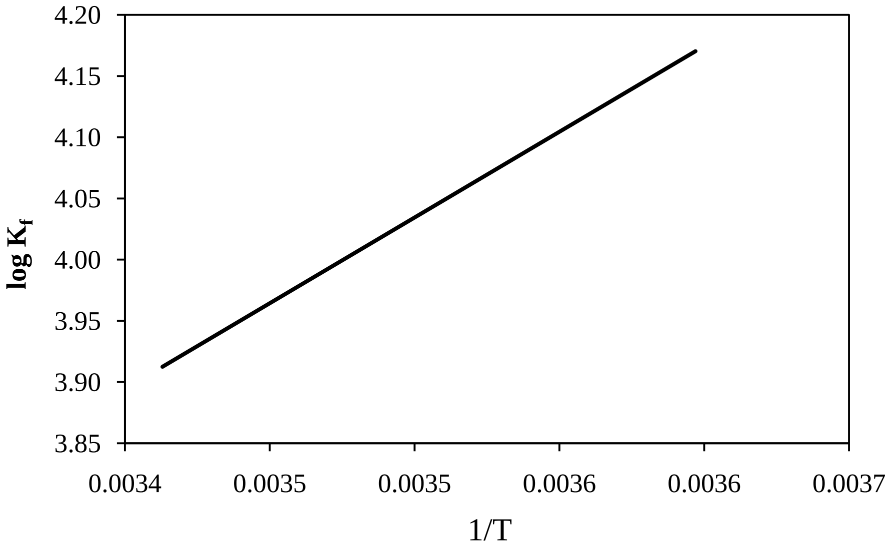

Fig.6 : The plot of $\log K_f$ vs. 1/T in dichloromethane solution.

Table 1 : Final log K_f and Є values at different temperatures in CH_2Cl_2

T	278	283	288	293
Log K_f in CH_2Cl_2	4.17±0.02	4.08±0.02	4.01±0.01	3.91±0.01
Log K_f in $CHCl_3$	6.08±0.04	5.99±0.01	5.91±0.02	5.84±0.01
є in CH_2Cl_2	7947±238	8549±256	9088±273	1186±336
є in CHCl3	3552±107	3927±117	4576±138	4912±147

Table 2 : Data due to determination of reaction order relative to TCNE in trichloromethane solution

TCNE/C222	**◌́Absorbance at 5°c**	**◌́◌́Absorbance at 10°c**	**Absorbance at 15°c**	**Absorbance at 20°c**
0.33	0.095	0.143	0.211	0.287
0.67	0.191	0.228	0.422	0.577
1.00	0.290	0.432	0.639	0.867
1.33	0.383	0.575	0.850	1.142

Table 3 : Data due to determination of reaction order relative to C222 in trichloromethane solution

C222/TCNE	**Absorbance at 5°c**	**Absorbance at 10°c**	**Absorbance at 15°c**	**Absorbance at 20°c**
0.33	0.098	0.151	0.211	0.295
0.67	0.195	0.302	0.442	0.640
1.00	0.293	0.461	0.668	0.878
1.33	0.391	0.611	0.892	1.181